THE PHASE RULE

A. C. D. RIVETT

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THE PHASE RULE

AND THE STUDY OF HETEROGENEOUS EQUILIBRIA

AN INTRODUCTORY STUDY

BY

A. C. D. RIVETT

M.A., B.Sc. (Oxon.), D.Sc. (Melb.)

ASSOCIATE PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF MELBOURNE

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PREFACE

THERE are many reasons why the study of heterogeneous equilibria has received insufficient attention in English-speaking countries. Of these, perhaps the chief is the unattractive nature of the experimental procedure involved in 'solubility work'. There is required so often a long series of quantitative determinations carried out strictly in accordance with a specified method. The discovery and perfecting of the method may have been of high interest: its application time after time is mere routine, and routine seldom makes appeal to an original mind. Few scientific investigators, particularly of the University class, can employ analysts who might be content to accept labour of this kind.

Then again the study of heterogeneous equilibria is one of those rather rare cases in which theory has outstripped experiment, and in which, moreover, theory has been built upon so firm a foundation that experimental confirmation or illustration often enough seems unnecessary. When there is so much of high significance in other sections of chemical science demanding experimental investigation as a preliminary to any theorizing, it is not surprising that heterogeneous equilibria find so few practical students.

There are circumstances, however, in which a certain path of laboratory investigation may rightly demand close

attention from chemists for quite other reasons than its intrinsic interest, and there can be no doubt that with respect to the study of heterogeneous systems such circumstances exist to-day. The immense waste of war must be made good as rapidly as possible, and as many methods of production of wealth must be employed as possible. The primary industries doubtless rank first in importance, but very near to them come the distinctively chemical manufactures. Of comparatively recent development even in the most advanced countries, and of only partial development in any country, these are destined to play a huge part, not only in making up for the losses resulting from the Great War, but also in determining the material positions of nations in the reconstructed world.

Now scarcely a single chemical manufacture deals solely with homogeneous systems. In the production of practically every chemical substance, organic or inorganic, several phases enter, usually liquid or solid, but often enough vaporous. It is a truism that the most efficient handling of them can result only from systematic study: yet it is a fact that such study has been given only in isolated cases to the heterogeneous equilibria of works practice. To the time factor in reactions attention is inevitably directed: but on the equally important side of equilibrium but little scientific study is expended. That for manufacturing a given article *a* process may be discovered without full laboratory investigation of the relations between the components and phases concerned has been often enough shown: but that *the one and only most*

efficient way of getting at the desired result will be discovered by 'hit and miss' methods is a mere matter of chance, and the odds are enormously against success. At the best success will always be delayed.

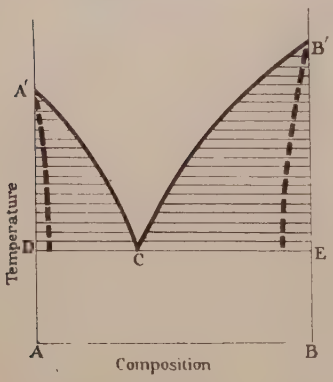
The study of heterogeneous equilibria, from the standpoints of the Phase Rule and the Principle of Le Chatelier and Braun, is one which every manufacturer would do well to require from his chemical staff. Whether or not costly evaporations are necessary, or recrystallizations, or extractions with solvents, only systematic work will show. The cost of such investigation will usually be slight compared with the gains that will be made possible.

The following pages give nothing but an introduction to the subject. They do not constitute either a treatise or a book of reference. The aim has been to discuss types of systems which may be met and ways in which such systems may be graphically represented, and to give some examples of the manner in which conclusions of practical importance may be deduced.

A difficulty immediately arises in presenting the subject in such a way that conclusions shall conform throughout strictly to the basic principles summarized in the Phase Rule. This difficulty must have confronted all teachers and will be obvious to the student after he has read a little of the subject. It is best illustrated by a specific simple example such as, say, that represented in the typical diagram, which may be found in any text-book at all on the Phase Rule, of a certain portion of a binary system, namely, that portion where temperature and phase com-

positions vary while pressure is maintained at such a value that vapour cannot form. The lines in the accompanying figure repeat the familiar representation, the details of which need not be discussed here.

The areas $A'DC$ and $B'EC$ are two-phase, univariant (condensed) systems. This means that if one arbitrarily assigns a value (within certain limits) to any one of the three variables, temperature, composition of liquid or composition of solid, the other two are single-valued constants of nature, and may not be varied consistently with the continued existence of the two-phase system. Hence, with variation in composition of liquids (solutions) along $A'C$ or $B'C$ there must be regular variation in composition of solids in equilibrium, and *vice versa*. This means, however, that the relations represented in the figure are impossible, since the figure implies that solid pure B, or A, may be in equilibrium not only with liquid of composition B', or A', but with any liquid at all along $B'C$ or $A'C$, respectively, as indicated by the tie-lines. In other words, arbitrary selection of the composition of the solid phase has not settled definitely and without ambiguity the temperature and composition of liquid at which alone the two phases



may continue to coexist. Strictly speaking, therefore, the lines giving compositions and temperatures of solid phases cannot be vertical. They must incline, however slightly, in the ways shown by the interrupted lines in the figure. This comes to the same thing as saying that there cannot be equilibrium between two phases unless each component is present in each phase, and in that form it is more or less axiomatic. A precisely similar argument may be applied to the region of two solid phases below *DCE*.

The fact that in an enormous number of cases the inclination of *A'D*, or *B'E*, is too small to be detected experimentally is usually taken as justification for neglecting this mere 'theoretical fact', and as a rule the case shown in the figure is considered to be quite distinct from one in which the slope of *A'D* or *B'E* is so great that experiment demonstrates it, or as it is more usually put, distinct from one where mixed crystals, or solid solutions, are formed. Actually there is no difference, except in degree. The case of solid solutions is the universal case, not only in binary, but also in higher, systems; the only one to be considered, strictly speaking, when principles are under discussion, as in a student's text-book.*

Nevertheless, one loses much from the didactic standpoint in entering upon the discussion of solid solutions at once. It is better to ignore at first the complications which they introduce. The customary method of treatment is the best, and it is followed here; but this can be justified only if the admission be definitely made that in such

* Cf. *Chemical News*, 1921, 123, 251.

treatment *any inevitable slight variation in the composition of the solid phase is deliberately left out of consideration.* Those cases where this decision involves more than a 'negligible' error from the experimental standpoint are considered in a cursory introductory manner in Chapter VIII, where further reference is made to the general question.

The student who is interested in heterogeneous equilibria should not fail to become familiar with the various developments worked out by Roozeboom, Schreinemakers, van 't Hoff, Meyerhoffer, Bancroft, Jänecke and many others, and described in numerous memoirs in chemical literature, particularly in the *Zeitschrift für physikalische Chemie.* The thermodynamic basis, primarily due to Willard Gibbs (*Scientific Papers*, i, pp. 62–100), will also amply repay study.

Of literature other than original memoirs in chemical periodicals, the most important is the standard work begun by Roozeboom and continued by Schreinemakers and others, though not yet complete, *Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre* (Vieweg und Sohn, Braunschweig). To this the author is very deeply indebted. He has made use of several of the typical diagrams contained in it.

Jänecke's *Gesättigte Salzlösungen* (Knapp, Halle a. S.) gives a concise account of the chief characteristics in an important though limited section; but certainly the best and most detailed treatment of the kind is to be found in Clibbens's *Principles of the Phase Theory* (Macmillan & Co.). Though this is too restricted in scope (dealing only with condensed systems) to be regarded as a suitable general

introduction for a student, it should be read by any one wishing to specialize in 'salt chemistry'. Findlay's *Phase Rule and its Applications* (Longmans, Green & Co.) covers considerable ground, especially in one- and two-component systems, though the omission of references to typical space diagrams showing the relations between all the variables in these respective cases makes it difficult for a student coming to the subject for the first time to obtain a clear idea of the correlation between all the projections and sections that are considered. Bancroft's *Phase Rule* is one of the earlier standard books, no longer readily obtainable, and a great deal that is fundamental will also be found in Ostwald's *Lehrbuch der allgemeinen Chemie.*

It is hoped that these chapters, based upon lectures delivered in the University of Melbourne in 1920, will aid in attracting students to an insufficiently cultivated field, especially those students whose later years may be devoted to the initiation and development of chemical manufacturing processes.

While taking sole responsibility for any errors that may be found in the book, the author has great pleasure in acknowledging his indebtedness to Professor Orme Masson, C.B.E., M.A., D.Sc., F.R.S., for the assistance and advice that have always been available to him; to Mr. E. F. J. Love, M.A., D.Sc., F.R.A.S., for very kindly reviewing the chapter dealing with certain matters of elementary thermodynamics; and to Mr. N. V. Sidgwick, M.A., Sc.D., F.R.S., for his interest while the book was in the press.

A. C. D. RIVETT.

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CHAPTER I

THE PHASE RULE

The term 'phase'. A portion of matter, homogeneous in the sense that its smallest mechanically isolable parts are indistinguishable from one another physically or chemically, was called by Willard Gibbs a 'phase'.

'We may call such bodies as differ in composition or state different *phases* of the matter considered, regarding all bodies which differ only in quantity and form as different examples of the same phase' (*Scientific Papers*, i. 96).

Homogeneity in the sense intended is a term applicable to a mixture of gases or to a solution of one substance in another. Mechanical methods, such as are effective in separating relatively large dissimilar masses, will be far too coarse to discriminate between molecules. A statement of homogeneity in such mixtures is parallel with a statement of definite temperature: in the latter case a thermometer is too big an instrument to show differences in temperature of individual molecules, though these undoubtedly exist.

Any phase will then be separated in space (the boundaries being quite definite) from every other homogeneous but different portion of matter. In the simplest case of all, that of a single chemical substance, it is clear in the first place that possible phases may be solid, liquid or gaseous. For every pure substance there must be at least these three phases capable of existence, though in some cases it may be beyond our means actually to realize the conditions of their existence. Since, however, numerous substances, such as sulphur, phosphorus and tin, may exist,

according to conditions, in different crystalline forms, that is, as distinct solids, it follows that for any single pure chemical species, three represents the minimum number of phases that may be expected, while the maximum number cannot be foreseen.

Specification of phases. To describe completely a single phase, whether solid, liquid or gaseous, of some one chemical substance, assuming effects (if any) of gravitational, electrical, magnetic and capillary (or surface) forces to be of a negligible order of magnitude, it is necessary and sufficient to state the volume occupied by unit mass, the pressure and the temperature.* Knowing these, it is possible always to reconstitute the system.

All our experience points to the conclusion that there will exist a relation between these quantities which may be expressed in the general form:

$$f(v, p, T) = 0,$$

although it may be beyond us in the present state of knowledge to give a precise statement of the relation in any particular case. Granting, however, that there will always be such a relation between volume, pressure and temperature, it is obvious that a knowledge of any two of these will suffice to give full information regarding the system, since the third will depend upon these two and be expressible in terms of them.

The term 'variable'. Since a particular phase may be able to exist under various conditions of pressure, temperature and specific volume, it is usual and convenient to

* Correctly speaking, the general relation between the volume, entropy and energy is required; for from it the relation between volume, temperature and pressure may be deduced, whereas the converse is not true. (See *Scientific Papers of J. Willard Gibbs*, Biog. Note, xv and xvi.) The more familiar course has been followed in the text.

refer to these factors, collectively, as the 'variables' of the phase.

Single phases of one component. Attention will first be confined to phases of one and the same chemical substance, and this substance will be termed the 'component'. A fuller discussion of the term will be given presently.

As just stated, the condition of a single phase is completely determined when any two of the three possible variables are specified, for the third is immediately settled in terms of these two by a relation $f(v, p, T) = 0$. If, however, only one of them be specified, an infinite number of pairs of values may be found for the other two which will satisfy the necessary relation. Hence in fixing the specification of the system one is free to select arbitrarily a value for one or other of the remaining two variables; this being done, the value of the third is also settled.

The term 'degree of freedom'. It is usual to say that such a system has one 'degree of freedom'. Actually the freedom is not, as implied, infinite: it exists only over a specific range, often very wide, but nevertheless limited. Thus, for a vapour under a given pressure, one's freedom in fixing upon a volume is curtailed by the fact that for certain volumes (and consequent temperatures) the substance under consideration may condense partially to a liquid. In fact, the 'freedom' of selecting at will a second variable is confined to those values of it under which the given chemical substance may continue to exist as, and only as, the single phase. The region of selection may be limited as regards both high and low values of the chosen variable; or it may be limited in one direction only. The determination of the limits of such selections, or boundaries of existence of specified phases, will occupy much attention in the sequel.

If, then, two variables, P and T, p and v or v and T, be given, a system consisting of a single phase is fully determined: if one only, there remains one choice before the determination. If none be given, then clearly two of the variable factors may be chosen at random (again within limits) before the system is adequately defined. But once two are selected, there is no further possibility of arbitrary choice: the third is settled and the system defined. Hence the maximum number of degrees of freedom possessed by a single phase of a homogeneous chemical substance is two.

Two phases of one component. Instead of considering an isolated single phase, consider next two in equilibrium with one another, each of the same chemical composition. These may be solid and vapour, liquid and vapour, solid and liquid or liquid and liquid. It is a conclusion from experience that two vapours never coexist in separate phases: all gases and vapours mix with one another in every proportion. Nor is any case on record of the existence, in equilibrium, of two liquid phases of one component.

Temperature and pressure must be the same in any two coexisting phases if there be equilibrium, but the specific volumes will not necessarily be alike. In this case there will therefore be two equations connecting pressure, temperature and volume, the first holding for the one phase and the second for the other. For brevity, such equations will be referred to as 'single-phase equations'.

Now, however, it becomes necessary to take into account yet another factor. Why does not the substance in one phase pass completely into the other, or *vice versa*? In short, why do the phases exist in equilibrium instead of amalgamating? Presumably the equilibrium is not static, but dynamic, and as many molecules pass in one second

from one phase to the other as from the other to the one. There must, then, be some condition, no doubt a function of the variables in the respective phases (though the precise nature of it is quite immaterial to the argument), which determines the equality of the tendencies of the phases to pass into one another.* This condition may be expressed in what one may term, for convenience of reference, a 'phase-equilibrium equation'.

Hence we have in the case of two coexisting phases of one component, three separate equations between the four variables, p, T, v_1 and v_2. It follows that if one variable be fixed, or in other words, one degree of freedom be exercised, the values of the other variables are settled and the system fully defined. It is not possible arbitrarily to give values to more than one variable, and so it may be concluded that the maximum number of degrees of freedom possessed by a system containing in equilibrium two phases of one and the same substance is one.

Condition as to magnitude of phases. It might be well to emphasize the assumption (implicit in the statement already made that capillary forces are taken as negligible) maintained throughout any discussion on the Phase Rule, namely, that so much of each phase is present in the system that the addition of more of it does not affect the equilibrium: or in other words, that the equilibrium is independent of the absolute or relative amounts of the two phases. This will be the case only when the phases are present in macroscopic masses; not when they are present in such minute amounts that the relative importance of the surface energy depends upon the state of division, as in fine drops of liquids or in crystals only a few microns in diameter.

* In this connexion, see Chapter VII for a brief account of what is known as 'chemical potential'.

Three phases of one component. Going further, consider a system of three phases in equilibrium. Again, temperature and pressure must be identical in all phases or obvious adjustments must occur: but specific volumes may differ so that there will be three equations (one for each phase) connecting the variables p, T, v_1, v_2 and v_3. In addition, there will be an equilibrium equation between phases I and II, and another between phases I and III. Since two phases, each of which is in equilibrium with a third phase, must be in equilibrium with one another (a statement often referred to as the *Law of the Mutual Compatibility of Phases*), it follows that the equilibrium equation of phases II and III will not be independent of these two. Therefore, between the five variables there are five equations. The values of these variables are thus completely settled in terms of the constants of the equations, and no freedom is left for arbitrary assignment of specific values to any of them. In a system of three phases of the same chemical substance there are not, then, any degrees of freedom. There is only one possible value for each of its five determining factors, and this is expressible in terms of definite natural constants.

Four phases of one component impossible. If four phases were in equilibrium, say two solids, liquid and vapour, it would follow from similar reasoning that between the six variables T, p, v_1, v_2, v_3 and v_4, there would be four distinct equations, one for each phase connecting its variables, and three phase-equilibrium equations; in all, seven equations, quite independent. The six variables could be calculated from six of the equations and the values so found would not fit in with a seventh entirely independent relation. Hence the coexistence of four phases of one and the same substance is an impossibility. Three is the maximum figure.

It has now been seen that in systems of one component we have, for one phase, two degrees of freedom to select variables consistent with the continued stable existence of the phase ; for two phases in equilibrium, one degree of freedom ; and for three phases, none. Also not more than three phases may coexist. These results may be expressed in the form

$$F+P=3$$

for any one-component, or unary, system, where P is the number of coexisting phases and F is the number of degrees of freedom possessed by the system. Examples will be discussed in Chapter III.

Two-component systems. If a single component can exist in at least three different phases, there would appear to be a considerable increase in the number of possible systems of coexisting phases when a second component is introduced. But actually the number is not great. For one thing, there can never be, or at any rate there never is, more than one vapour phase : many liquids, too, are miscible in all proportions, while some others which might be only partially miscible, such as water and molten salt, may not both be able to exist liquefied in the same temperature range : some pairs of solids, too, are miscible and so may form one phase instead of two. But, besides these limitations there is another, similar to that already found in the case of one component.

One phase of two components. As the simplest case, assume that two components, say salt and water, form only one phase, a homogeneous solution. To define this solution it is necessary to state its temperature, the pressure exerted upon it, and the specific volume of each component. Instead of dealing further with specific volumes, there will now be adopted the more usual practice of taking concentrations.

Specific volume is the volume occupied by unit mass; concentration is mass in unit volume. One cubic centimetre (or any other selected unit of volume) will contain c_1 grammes of the first component and c_2 of the second; and c_1 will not be expressible in terms of c_2 unless the density of the phase be known. Thus, of the three quantities c_1, c_2 and density, two will always be independently variable, and these will be taken to be c_1 and c_2.

There are now four variables, p, T, c_1 and c_2, and only one equation, of the single-phase type, between them. Obviously then, three of the four variables may be fixed arbitrarily without violating the necessary condition of the equation which at once fixes the fourth in terms of these three. Where two components are concerned there are thus three degrees of freedom possessed by any system containing a single phase.

More than one phase of two components. Similarly when two phases, each containing the two components, coexist, there will be two single-phase equations and one phase-equilibrium equation for each component: four equations in all between the six variables p, T, c_1, c_2, c_1' and c_2'. It follows that the freedom of selection of variables consistent with the continued coexistence of the two phases is limited to two: the remaining four are then determined in accordance with the equations quoted. Thus, the number of degrees of freedom possessed by a two-component system in two phases is two.

With three phases there will be eight variables, p, T, c_1, c_2, c_1', c_2', c_1'' and c_2'' (where dashes denote phases in an obvious manner), and seven equations, three being of the one type and four of the other. There remains, therefore, only one degree of freedom where three phases coexist.

So, too, where there are four phases, there will be ten variables, namely, p, T and two concentrations in each of the four phases. Between the variables there will be four single-phase equations and six phase-equilibrium equations. So that every one of the variables will be expressible in terms of the natural constants of the equations, and no freedom for arbitrarily fixing any one of them will remain. There are, then, no degrees of freedom in a system containing two components in four phases.

From the coexistence of five phases we should, by similar reasoning, obtain thirteen independent equations between twelve variables. This is impossible: hence the supposition of the existence of five phases in equilibrium cannot be maintained. Four is the maximum number.

Putting all these facts together, it is clear that in two-component systems $F+P=4$.

The term 'component'. Now in any two-component system it is possible that besides the two components and homogeneous mixtures of them in the solid, liquid or vaporous state, there may exist definite chemical compounds which, being chemically distinct bodies, might reasonably be ranked as new or additional components. There is, as a matter of fact, no particular reason why they should not, except the very good reason of convenience and simplicity. It is obvious that the composition of a compound, say a salt hydrate, can be expressed in an equation involving definite quantities of its components only: and so for every equation involving concentrations of the former a precisely equivalent one in terms of the latter may be deduced. For a given system, in short, the difference between variable factors and equations connecting them will remain the same if a compound existing in it be considered a component additional to its two constituents, for

the number of variables and the number of equations will be increased equally.

It is clearly an advantage to refrain from this quite useless increase of variables and equations and to restrict the number of each to a minimum, thus maintaining complete independence among the equations. This may be done by adopting the rule that no compound occurring in a system will be regarded as a new component unless its composition be such that it cannot be expressed in terms of a minimum number of components already selected. In Nernst's words, one must take as the number of components in a system the minimum number of molecular species in terms of which the compositions of all phases in that system may be quantitatively expressed. The selection of the components obviously leaves room for arbitrary decision: the selection of the number does not.

In case there may be difficulty in deciding this really quite simple matter the following general rule will always give the information desired:

> From the total number of distinct chemical (molecular) species in the several coexisting phases subtract the number of chemical equations required to express the changes which may occur when equilibrium is disturbed. The remainder is the number of components in the sense desired.

Example of determination of number of components. As an example which may be helpful to the student, take the system in which there may exist, according to circumstances, the following chemical species:—Calcium oxide (CaO), water (H_2O), carbon dioxide (CO_2), calcium carbonate ($CaCO_3$), calcium hydroxide [$Ca(OH)_2$], carbonic acid (H_2CO_3) and calcium bicarbonate [$Ca(HCO_3)_2$]. Here there are seven distinct molecular species. Between them

we have the following equations, which suffice to express the changes which may occur when equilibrium is disturbed:

$$CaO + H_2O \rightleftarrows Ca(OH)_2$$
$$H_2O + CO_2 \rightleftarrows H_2CO_3$$
$$CaO + CO_2 \rightleftarrows CaCO_3$$
$$CaCO_3 + H_2CO_3 \rightleftarrows Ca(HCO_3)_2.$$

The difference between the number of molecular species (seven) and the number of equations (four) is three. If one increase the number of species by including ions, then there will be an exactly equal increase in the equations. The system is therefore one of three components.

Since for the expression of compositions of phases it is quite immaterial in terms of what particular substances the expression is made (indeed, we often do not know exactly what molecular or ionic species are present) so long as all the matter in the phase is accounted for, it follows that any three species may be selected as the components provided that the composition of any one of them cannot be stated in terms of the other two. In the case cited, the most natural choice would no doubt be calcium oxide, carbon dioxide and water; for it is at once clear that the other four species may be regarded as composed of these in pairs, or altogether, as the case may be. But the same holds for other choices. Thus, taking calcium carbonate, calcium hydroxide and calcium bicarbonate as components, the other possible constituents of phases may be expressed in terms of them thus:

$$H_2CO_3 = Ca(HCO_3)_2 - CaCO_3$$
$$2CO_2 = Ca(HCO_3)_2 - Ca(OH)_2$$
$$2H_2O = Ca(OH)_2 - 2CaCO_3 + Ca(HCO_3)_2$$
$$2CaO = 2CaCO_3 + Ca(OH)_2 - Ca(HCO_3)_2.$$

Generalization. Having now defined strictly all the terms that will be used, and having considered in detail the various possibilities in the two simplest types of system, one may proceed to obtain a general statement of the relations in any system between number of phases, number of components, number of variables and number of independent relations connecting them, the difference between the two latter (if any) being the degrees of freedom of the system.

Suppose that P phases exist in equilibrium with one another and that their compositions may all be expressed in terms of C components. For each phase there will be an equation connecting its variables, pressure, temperature and concentrations; that is to say, there will be P single-phase equations. Also, the P phases may be arranged in $P-1$ pairs, so that there will be $P-1$ phase-equilibrium equations for each component, or $C\,(P-1)$ altogether.

The total number of equations is thus $P+C\,(P-1)$.*

The variables will be pressure, temperature and the concentration of each component in each phase; altogether, $C \times P$ concentrations. The total number of variables is thus

$$2+CP.$$

Representing by F the difference between the number of variables and the number of equations connecting them, that is, the number of degrees of freedom of the system, we have

$$F = (2+CP)-[P+C\,(P-1)]$$
$$= 2-P+C,$$

or

$$F+P = C+2.$$

* It must be remembered that concentrations are assumed to be expressed in quantities of matter per unit volume. If an expression in fractions of an arbitrarily specified total mass be preferred, the argument takes a slightly different form, though the conclusion is, of course, the same. Compare Partington, *Proc. Chem. Soc.*, 1911, p. 13.

This very simple relation is what is termed the *Phase Rule*. The conclusions already obtained in the earlier consideration of certain simple systems, namely, $F+P=3$ and $F+P=4$, are at once seen to be the special cases in which $C=1$ and $C=2$, respectively.

Nomenclature. It is convenient when referring to systems to adopt a nomenclature as brief as possible, and it has become customary to describe any system first in terms of the number of components present, and then in terms of the number of degrees of freedom possessed by it.

Thus, for systems of one, two, three, four, five (and so on) components, one uses the terms unary, binary, ternary, quaternary, quinary (and so on), respectively. When $F=0$ the system is said to be invariant, since none of its variables may be altered at will without destroying the system in the sense of altering the number of coexisting phases. If $F=1$, the system is univariant; and we have, in order, the terms bivariant, tervariant, quadrivariant, quinvariant and so forth.

CHAPTER II

THE PRINCIPLE OF LE CHATELIER AND BRAUN

If a system in equilibrium be subjected to an alteration in one of the factors conditioning the equilibrium, it is clearly a matter of importance to be able to state, qualitatively at any rate, in what direction displacement will occur if and when the system attempts to accommodate itself to the new condition. A generalization making this

possible was put forward in 1885 by Le Chatelier, and independently in the following year by F. Braun. It was based solely on experience and has proved to be quite general in its application, being in fact covered by the Second Law of Thermodynamics.

Illustrations of the principle. The nature of the law is best seen from specific examples. Suppose that a system in equilibrium, say liquid water and water vapour, in a fixed space and at a certain temperature and pressure, be supplied with a definite amount of heat. If no change take place in the system there will be a rise in temperature, dependent only upon the quantities and specific heats of the liquid and vapour. If, however, change occur spontaneously and a new equilibrium condition be attained, it will be found that the rise in temperature is less. The consequence of adding heat, namely, rise of temperature, has been lessened by the process of adjustment of equilibrium between the phases. In this particular case some of the heat has been used to cause evaporation of a certain amount of water, the vapour pressure of which is thereby increased: the remainder alone has been available to increase temperature.

Similarly, if the volume available to the two phases at a fixed temperature be reduced to a specified extent, there will be, if the phases remain otherwise unaltered, an increase in the pressure exerted by the system. But, if change occur and a new equilibrium be attained with different relative amounts of liquid and vapour, the increase in pressure will be less. The alteration of the relative amounts must therefore have been one involving decrease in volume, that is, condensation of vapour.

Or again, if solid and liquid be in equilibrium in a certain space and the volume of the system be reduced

a fraction by compression, the resultant pressure will be greater when the relative amounts of each phase remain constant than it will be if these amounts adjust themselves naturally. The lower pressure in the latter case can only be the result of an adjustment involving a decrease in volume. If on melting the solid expands then more solid must have been formed: if it contracts then some must have melted.

General statement of principle. In all three cases we have the same general rule. Given a change in the conditions under which a system is in equilibrium, the consequent alteration in the factors which specify the system will always be less for a change to a new state of equilibrium than for a change in which the system remains otherwise as before.

It is essential, however, to be more precise in speaking of changes and alterations in the factors of a system so that cases may not occur in which there is ambiguity. When, for example, a gaseous system is subjected to adiabatic compression, its temperature is raised; that is to say, the translational energy of its molecules is increased, and therefore the pressure exerted by them is also increased. Hence the spontaneous change in the system, development of heat, has tended to intensify the initial increase of pressure, in apparent contradiction to the general statement just made. It therefore would seem that some more precise formulation of the principle is required: pressure and temperature are evidently not the factors to be considered in a case such as this.

This formulation may best be arrived at by emphasizing the distinction between intensity and quantity factors respectively. Pressure, for example, is an intensity factor; volume is the corresponding quantity factor. Temperature

and entropy stand in a similar relation; so do electromotive force and electric current, surface tension and surface, osmotic pressure and volume occupied by unit mass of the solute (dilution). The variables temperature and pressure which enter so largely into the considerations which follow are thus both intensity factors.

Now the product of the intensity factor and the corresponding quantity factor is always of the dimensions of energy, and if changes be brought about in the quantity factors, say, and be represented by dq_1, dq_2, ... dq_n, the total change of energy dE will be given by

$$dE = I_1 dq_1 + I_2 dq_2 + \ldots + I_n dq_n,$$

where I_1, I_2, ... I_n are the corresponding intensity factors.

When, then, systems are subjected to stresses or strains of any kind, it is to the relations between corresponding intensity and quantity factors that attention must be directed.

Precise statement of principle. The principle may now be expressed definitely and without possibility of ambiguity in the following way:

> Any alteration in an intensity factor I, consequent upon a given alteration dq in the corresponding quantity factor, will be smaller for a change to a second state of equilibrium (with consequent adjustments of other factors) than it would be if all the other quantity factors were to remain constant.

The same thing is, of course, intended to be conveyed by the more usual statements of the rule, as, for example, that every system in equilibrium is conservative; that a system tends to change in such a way as to oppose and partially to annul any alteration that may occur in a factor; that if a system in equilibrium be subjected to a constraint

by which the equilibrium is shifted, a reaction takes place which opposes the constraint. Such statements, however, are certainly not sufficiently specific.

The principle of Le Chatelier and Braun is only qualitative, and thus enables us to predict only the direction in which the variables of a system will change when one of them is altered. By the aid of the laws of thermodynamics quantitative expressions embodying it may be deduced: but for the present it suffices to retain the qualitative result. Instances in accordance with the rule will occur repeatedly in the sequel.

For a more adequate discussion the student is referred to papers by Ehrenfest (*Zeit. phys. Chem.*, 1911, **77**, 2) and Lord Rayleigh (*Journ. Chem. Soc.*, 1917, **111**, 250).

CHAPTER III

ONE-COMPONENT SYSTEMS

The Phase Rule, as deduced in Chapter I, deals with the number of factors concerned in defining equilibrium, and it is apparent that in studying the application of the rule to specific cases we shall be dealing primarily with the interdependence of these factors. In any one-component system the number of factors, or variables as one may continue to call them, the values of which determine the equilibrium, is three, these being temperature (T), pressure (p) and specific volume (v). The latter, volume in which unit mass is contained, may of course be replaced by density, or mass present in unit volume.

To show the interdependence of the three variables in a given one-component system a graphical representation in three dimensions will be necessary, and the immediate consideration of a typical space model is probably the best introduction to the particular cases to be studied.*

A typical 3-dimensional model. It is not possible to give one general model which will represent rigorously the relations of p, v and T in all one-component systems, since the relative positions of some of the regions mapped out vary according to certain characteristic properties of the component. But the alterations involved are readily made; and Figure 1 (taken from Jänecke, *Gesättigte Salzlösungen*, p. 11), which represents in perspective, quite diagrammatically, p, v and T for a one-component system such as that of water, where at the freezing-point $v_{vapour} > v_{solid} > v_{liquid}$, may be taken to be typical, though it will require an obvious adjustment to make it applicable to the more frequent case, such as that of alcohol, where $v_{vapour} > v_{liquid} > v_{solid}$.

The three-phase system. As a starting-place in description of the model, it is convenient to take the points a, b and c which give the specific volumes of liquid, solid and vapour, respectively, at the particular temperature and pressure at which they coexist. The line abc is therefore at right angles to both pressure and temperature

* This would appear not to be the general view of teachers writing on the subject. It is customary to deal only with plane diagrams, i.e. sections and projections, showing relations between two only of the three possible variables, the two most favoured in one-component systems being temperature and pressure. Such figures will be dealt with here in their turn, but it is considered that from a didactic point of view it is a distinct advantage to start from the complete model, and to obtain from it the partial representations of the various possible two-dimensional figures. A similar course will be followed in the higher systems.

axes. It is needless to say that in any particular case, such as that of water, the length *ab* would be very much less, relatively to *ac*, than it is shown to be in the figure.

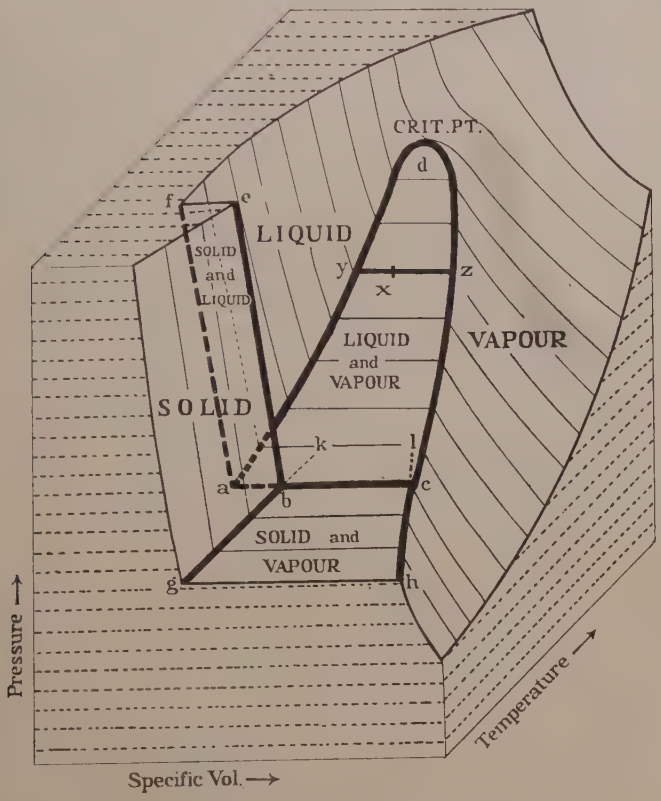


FIGURE 1.

Actually, for water, *a* corresponds with a value $v = 1{\cdot}000132$ cubic centimetres; *b* with $v = 1{\cdot}0917$; *c* with $v = 210$ litres. The whole model has been distorted in order to bring out with sufficient clearness its different divisions.

Since along the line *abc* there are three phases coexistent, it follows from the phase rule, since $C = 1$, that $F = 0$. One may not, therefore, alter any of the conditioning factors. The system is invariant. To attempt to effect any alteration would result in the disappearance of one of the phases. Attempted pressure increase would cause the disappearance of the vapour phase; persistent attempt to raise the temperature would result in the solid disappearing; and so on. The pressure and temperature of coexistence of solid, liquid and vapour in a one-component system are single-valued constants of nature, and so are the respective specific volumes.

In the water system the value of the pressure is 4·6 millimetres of mercury; that of the temperature is +0·0076° C.; the volumes have been quoted above.

The term 'pressure'. It is necessary to be quite clear about the meaning attaching to the term 'pressure' in such a case as this. It must be understood to mean that pressure which the vapour phase (and the other phases) of the component exerts, and is on no account to be confused with such a total pressure as may be exerted through, say, the agency of some other substance, or mixture of substances, such as air. Unless this be borne in mind there will be difficulty in reconciling the invariance of the three-phase water system with the facts underlying the commonly quoted but inaccurate statement that the three phases, ice, liquid water and water vapour, may coexist at other temperatures if confined in a vessel also containing air or other gas, the pressure upon which is varied. Thus, it is often said that these three phases coexist at 0° C. under a total pressure, exerted partly by the water vapour and partly by the atmosphere, equal to 760 mm. of mercury; or at −0·059° C. under 8·1 atmospheres, or −0·129° under

16·8 atmospheres. Actually they do nothing of the kind.

For if one considers the equilibrium relations of the system *abc* of Figure 1, one is led to the conclusion that the only possible way of altering the pressure on the system is by introducing a new component; most simply, a gas. There is no other way of changing the pressure from 4·6 mm. while maintaining the coexistence of three phases. In the simplest case, where the new component is a pure gas, the system will, however, at once become one of two components, or binary: if the gas be a mixture, the system may, and usually will, become of a still higher order. Corresponding with the increase of components there will be an increase in degrees of freedom, and at once it becomes apparent that three phases may be in equilibrium at other values of the variables than those represented at *a*, *b* and *c*. These phases, though, will not be ice, liquid water and water vapour; they will be ice saturated with the new gaseous component (for that solids may dissolve gases, however slightly, can hardly be denied), liquid water also saturated with it, and a vapour phase which will be a mixture of water vapour and the gas. These are three phases belonging to a two-component system, having therefore one degree of freedom, and are quite different from the three phases of the invariant one-component system.

One cannot neglect the gas as a component, terming it 'neutral', for while its solubility in both solid and liquid phases may be so slight as to seem quite negligible and to justify the term 'neutral', at any rate from a practical standpoint, its 'solubility' in the third phase, vapour, will of course be infinite.

The two-phase system: liquid and vapour. Suppose now that in the three-phase system represented at *a*, *b* and *c* in

Figure 1, an attempt be made to raise the temperature of the three phases by applying heat. It will be found that the ice will melt, for experience has shown that under no circumstances yet discovered may ice be heated above 0·0076° C. in presence of both liquid and vapour. A transfer of matter from one phase to another, or a phase reaction, will take place. In melting, the ice will absorb heat, and if there be sufficient ice and only a limited supply of heat, the attempt to alter the temperature of the system may fail to do more than change the proportions of ice and liquid. This is a case with which Le Chatelier's theorem is clearly in accord. If, however, the application of heat be persisted in, all the ice will melt before the temperature begins to rise, and only when liquid and vapour are the sole phases remaining can a value above 0·0076° be reached.

At the moment when the whole of the ice has just disappeared the system is represented by the two points a and c of Figure 1. It is a one-component system in two phases, so that $F = 1$. Without altering the phase equilibrium one may (within limits) arbitrarily vary one condition of the system, either pressure or temperature. This of course includes alteration of specific volume, since there is no other way of doing this than by altering pressure or temperature. But when one freedom of choice has been exercised, say a particular temperature selected, the remaining conditions, p and v, adjust themselves accordingly and cannot be varied without bringing about the disappearance of one of the phases.

Suppose that the temperature be that corresponding with the line yz. The vapour pressure will increase to a particular value which may be read from the model. The specific volume of the liquid will increase or decrease

according to whether the expansion due to rise of temperature be greater or less than the contraction due to increase of pressure. It is probably an invariable rule that the coefficient of expansion by heat is greater than the compressibility due to corresponding alteration of vapour pressure, so that the volume at y will be greater than that at a. On the other hand, the specific volume of the saturated vapour at the higher temperature will be less than that at the lower, for the effect of increased temperature in expanding the vapour is far more than compensated by the greater amount of vapour per unit volume required for equilibrium with the liquid. The length of yz is therefore less than that of ac, or, in other words, with rise of temperature the specific volumes of vapour and liquid approach one another. At a sufficiently high temperature (and pressure) they may be expected to become equal, and such a point is shown in the diagram at d.

The critical point. One cannot say that at this point the one or the other phase has disappeared, but simply that the two phases have become indistinguishable from one another. Each contains the same amount of the same component in the same state in each cubic centimetre, and this implies identity in all respects. This point is always known as the critical point, and the three factors as critical pressure, critical temperature and critical volume, respectively. For the water system, the approximate values are 195 atmospheres, 360° C. and (for one gramme) 4·8 cubic centimetres.

Limits of liquid-vapour system. The continuous curve *aydzc* gives all the values which p, T and v (or rather, v_1 and v_2) may assume consistently with the continued coexistence of liquid and vapour. If the endeavour be made to subject the two-phase system to a pressure or temperature

not corresponding with this bounding line, one phase or other will disappear; and that is why, when it was stated that the vapour-liquid system possessed one degree of freedom, care was taken to make it clear that this freedom was not infinite, but that its exercise was restricted to certain limits. The curve *aydzc* gives the precise definition of these limits in the present case.

Any point in the area bounded by this curve and the straight line *ac* will give an average specific volume of two phases coexisting in certain proportions. Thus the point *x* gives for a particular temperature and pressure the mean specific volume of a mixture of liquid and vapour in which the fraction *xz/yz* is liquid of specific volume corresponding with the point *y*, and *xy/yz* is vapour of specific volume corresponding with the point *z*. The area *aydzc* is thus the field of coexistence of liquid and vapour, or the area of the univariant system.

The two-phase system: solid and liquid. Returning to the line *abc* of the invariant system, assume this system to be subjected to persistent infinitesimally increased pressure on the vapour, instead of increased heat-supply. Vapour will condense in the endeavour to reach the lower equilibrium pressure and escape the restraint, and ultimately it will disappear as a separate phase. There will thus be none of the component remaining in the condition corresponding with the point *c*, and the other two phases of liquid and solid will be represented by *a* and *b*. Again, therefore, the attempt to exercise a degree of freedom upon the three-phase system has produced a two-phase system, and this may be subjected to one factor arbitrarily chosen (within limits) without further alteration in the number of phases.

The conditions governing the equilibrium between solid and liquid have been examined in detail for only a few sub-

stances. The specific volumes of both phases will in general be decreased by increase of pressure, that of the liquid more so than that of the solid. But whether increase of pressure will raise or lower the temperature of coexistence of the two phases, conveniently called the melting-point, depends upon the relative values of the specific volumes. When the solid, on melting, contracts, increase of pressure will, in accordance with the rule of Le Chatelier and Braun, bring about that change, namely, diminution of volume, which tends to relieve the pressure. The solid will therefore liquefy more readily, that is, at a lower temperature. If, on the other hand, the solid expand on melting, increase of pressure will raise the melting-point. The latter case is by far the commoner: the former holds for a comparatively small number of substances, including water, potassium nitrate, bismuth and cast iron.

The precise directions of slope of the curves *be* and *af* will therefore depend upon the nature of the component. There is not necessarily any limit to the course of these curves with increasing pressure, except the limit imposed by difficulties of experiment. The area *abef* may then be regarded as a portion of that of the two-phase system containing liquid water and ice.

Improbability of solid-liquid critical point. There has been much interesting speculation as to whether a critical point be possible between solid and liquid phases similar to that at point *d* in Figure 1 between liquid and vapour. Without going into details it may be pointed out that there is a fundamental difference in the two cases which rather weakens any argument from the one to the other by analogy. In both liquid and vapour phases the molecules are without order in arrangement. The phases differ in the average distances between molecules and in other properties dependent

thereon, so that a continuous passage from one state to the other is readily conceivable.

In a solid, on the other hand, the molecules are arranged in definite geometrical order (if indeed one may regard the solid structure as composed of separate molecules at all), and to picture a continuous passage from that to the disorder of a liquid is a little difficult. The possibility of a solid-liquid critical point is, to say the least of it, rather doubtful.

The two-phase system : solid and vapour. One other change from the three-phase system *abc* to a two-phase system is possible. If an attempt be made to lower the temperature, water will solidify in the attempt to restore the invariant conditions : but persistent removal of heat will result in the complete disappearance of liquid. At the moment of its disappearance, if the cooling has been infinitely slow, the system will be represented by the two points *b* and *c* for solid and vapour respectively. This system has one degree of freedom, and temperature or pressure may be varied arbitrarily, within limits, without destroying it. On lowering the temperature, the specific volume of the ice will steadily decrease along the curve *bg*, though only slightly.

The equilibrium vapour pressure will decrease and the specific volume of the vapour will increase as shown by the curve *ch*. The two curves *bg* and *ch* therefore diverge from each other with decrease of temperature. The decrease of vapour pressure with temperature in the region of the point *c* is greater per degree for ice than for water : hence the curve *cl*, which is *hc* produced, would lie above the curve *cz*, and conversely *zc* produced would lie above *ch*. The lower limits of the curves *bg* and *ch* will be reached only at the absolute zero of temperature : the vapour pressure will then be zero, which means that the specific volume of the vapour approaches infinity as the zero tem-

perature is reached. The volume of the solid will have a definite value.

Within the region bounded by *bc* and the curves *bg* and *ch*, or their continuations, the conditions are such that the one component must always exist in two phases, solid and vapour. Any attempt to impose conditions corresponding with points outside this area will effect the change of one phase into the other, giving a single-phase system with two degrees of freedom.

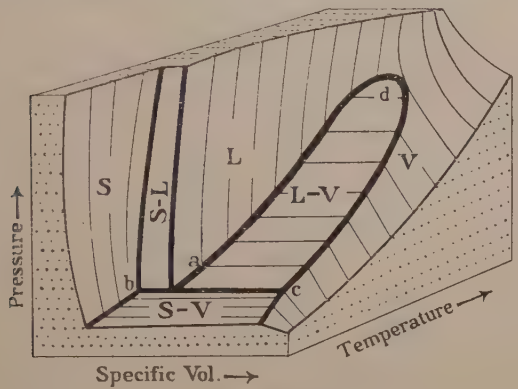


FIGURE 2.

Single-phase systems. There are three such single-phase systems, the relative positions of which are shown in Figure 1 by the areas marked solid, liquid and vapour, respectively. The liquid and vapour areas merge into one another above the critical point: but there is no evidence in the case of water of a similar merging of ice and vapour areas or of ice and liquid areas. A critical point (unstable) between ice and vapour is improbable for the same reasons that make one between ice and liquid seem unlikely.

To turn Figure 1 into a diagrammatic representation of a one-component system in which $v_{solid} < v_{liquid} < v_{vapour}$

only a slight adjustment of the relative positions of the areas is required, and Figure 2 indicates the change required.

Summary. Summarizing what has been said of Figure 1 (and, *mutatis mutandis,* the same applies to Figure 2), all realizable equilibrium associations of the variables T, p and v may be represented for a one-component system on certain surfaces and their intersections at lines or points. Any values of p, T and v represented by points not lying on these surfaces or their intersections cannot belong to a stable phase or to phases in stable equilibrium. Metastable equilibria are possible in some cases, but the present discussion is not concerned with them.

Of the areas, those marked solid, liquid and vapour, respectively, are systems of a single phase and bivariant: those marked solid and liquid, solid and vapour, and liquid and vapour are systems of two phases and univariant. The latter areas differ from the former in that they are plane in one direction, the ends of lines (which may be termed conjugation lines) in this direction giving the values of the variables for the respective coexisting phases. Finally, the points a, b and c represent together a three-phase or invariant system.

Projection on p-T plane. Now consider this three-dimensional figure from certain more restricted points of view. One of these leads to the diagram, reproduced in Figure 3, which is usually given to represent the one-component system water.

Pressures are plotted on the axis of ordinates and temperatures on that of abscissae. If this figure be considered in relation to Figure 1 it will be seen that it is simply the orthogonal projection of the space model on the pressure-temperature wall. This comes to the same thing as regarding it as Figure 1 in which the volume axis has been taken

with such huge volumes corresponding with unit length, that differences in volume of the order dealt with are beyond the possibility of representation as finite distances.

The three points *a*, *b* and *c* now become one at *A*, and hence to this is always given the name of 'triple point'. Points such as *y* and *z*, *e* and *f*, *g* and *h*, fall together at *Y*, *E* and *G*, respectively. The line of the three-phase system has become a point: the areas (plane in one direction) of

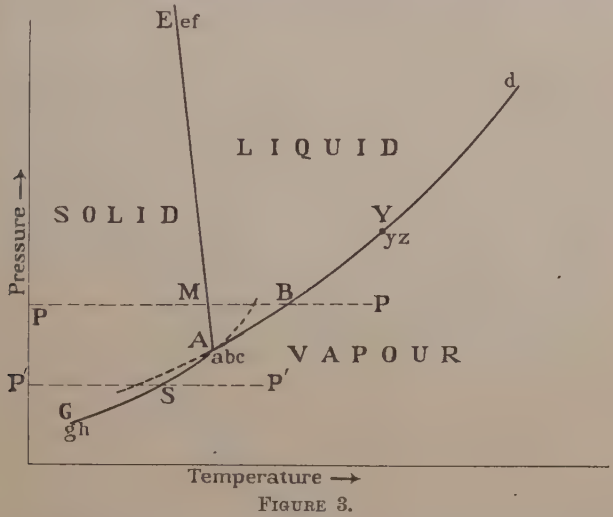


FIGURE 3.

the two-phase systems have become lines: the areas of the single-phase systems remain areas, but are now plane.

The curve for the liquid and vapour system begins at *A* and ends sharply at *d*, the critical point. The solid-vapour curve *AG* will end at zero pressure and zero (absolute) temperature. The end of the solid-liquid curve *AE* cannot be predicted. The complications in it in the case of water are shown in their pressure-temperature relations in Figure 4, where the division of the field, so far as investigated,

between liquid and the various solids, Ice I, Ice II, Ice III, Ice V and Ice VI, is clear. In interpretation, this figure offers nothing new as compared with Figure 3.

The slope of the curve *AE* in Figures 3 and 4 towards the pressure axis is in accordance with Le Chatelier's theorem and the fact that ordinary ice (or Ice I), on melting, contracts in volume. If the volume change were in the opposite direction the curve would slope away from the pressure axis. Examples of this are seen in the curves *BD*, *DF* and *FH* of Figure 4.

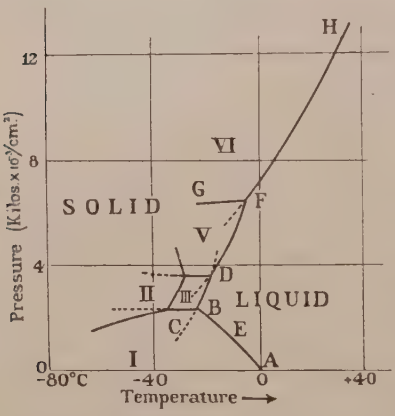


FIGURE 4.

Phase relations at atmospheric pressure. One small point frequently appearing in practice may be illustrated from Figure 3. The value of p at the triple point *abc* will be different for different substances. It may be, and for most common liquids like water is, below the atmospheric pressure of 760 mm. of mercury represented by the horizontal line *PP*. It is clearly possible in any such case to obtain the three phases, in pairs or singly, in systems of varying temperature open to the atmosphere. Thus, on applying heat to the solid, it melts at *M* and the liquid boils at *B*.

But there are other cases, exemplified by ammonium chloride and carbon dioxide, where the 760 mm. pressure line, represented now by *P'P'* in Figure 3, lies below the triple point, cutting only the vapour-solid curve *GA*. In such cases, liquid cannot be obtained in equilibrium experi-

ments unless means be taken to raise the pressure above that of the atmosphere. The only possible change for the solid, if heated, is to vaporize at S: conversely, vapour, if cooled, condenses directly to solid. These phenomena, in sequence, make up the process of sublimation.

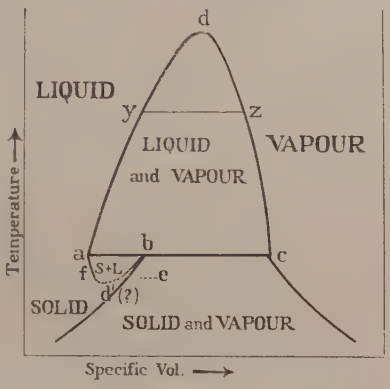


FIGURE 5.

Projections on v-T and p-V planes. Returning again to Figure 1, it may be seen that two other two-dimensional projections, besides Figure 3, may be obtained, namely, those on the volume - temperature and the volume-pressure planes, respectively. The former is shown diagrammatically in Figure 5.

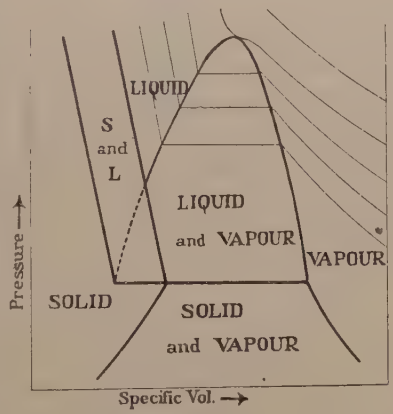


FIGURE 6.

The region *abef* of coexistence of solid and liquid is very small on account of the slight upward slopes of the curves *be* and *af*. This area will become closed similarly to that of *abcd* for liquid and vapour only in the unlikely event of there being a liquid-solid critical point *d'*.

The remaining projection is given in Figure 6. An actual example of this, commonly quoted in text-books, is Andrews's pressure-volume diagram for carbon dioxide.

This projection involves the partial superposition of the solid-liquid and liquid-vapour fields. For the rest, both it and Figure 5 should be readily intelligible if the discussion of Figure 1 has been followed. A few isothermal lines have been drawn in Figure 6: similarly isobars might be drawn in Figure 5 and isochors in Figure 3.

Possibility of additional phases. Although no single component can exist in two distinct vaporous forms constituting separate phases, it is quite possible for two or more distinct solid, or even liquid,* phases to appear. In such cases there will be additional divisions in the p, T, v model to represent the conditions in which the added possible one-, two- and three-phase systems may exist. There will not, however, be anything in such systems essentially different from what has already been sketched in Figure 1. If, for example, a component may exist in four phases, say two different solids, liquid and vapour, represented respectively by S_1, S_2, L and V, then there may exist according to conditions four one-phase systems, six two-phase systems, viz. S_1-S_2, S_1-L, S_2-L, S_1-V, S_2-V and $L-V$, and four three-phase systems, viz. S_1-S_2-L, S_1-L-V, S_2-L-V and S_1-S_2-V. But there will not be a system S_1-S_2-L-V in which all four phases coexist, for such a system would require, in accordance with the Phase Rule, $F+P=C+2$, that there be a negative degree of freedom, and that is meaningless.

Hence further cases of one-component systems introduce nothing more than repetition of areas, lines and points

* As a matter of fact no case has yet been found of a single component existing in two distinct isotropic liquid phases.

similar to those of Figure 1. It will therefore suffice to indicate by means of projection diagrams the complications introduced, and for this the most convenient is that on the pressure-temperature plane.

One component giving S_1, S_2, L and V. Figure 7 represents diagrammatically the one-component system of sulphur, which substance, besides giving liquid and vapour

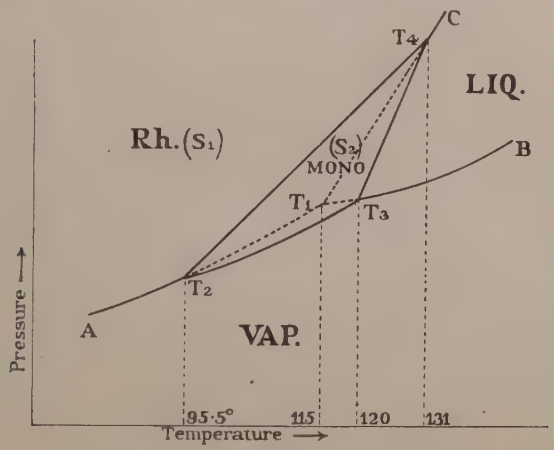


FIGURE 7.

phases, may exist according to conditions either as a rhombic or a monoclinic solid.*

The curve AT_2 is that of the two-phase system rhombic

* Many complications appear in an experimental study of sulphur, owing to its marked capacity for forming molecules of varying complexity and to the fact that equilibrium between these is not always attained rapidly. Unless an investigator be quite certain that he has attained equilibrium, he is not justified in regarding the system as unary: it becomes binary or of a still higher order. The use of the term 'pseudo-binary' in this connexion is now common. Many other one-component systems offer the same difficulties experimentally as does sulphur.

solid and vapour. If a second form did not exist, one would expect this curve to continue to a triple point T_1 at which liquid would appear and from which two curves T_1B and $T_1'C$ would run, representing liquid-vapour and rhombic-liquid systems, respectively. But actually, if perfectly stable systems alone be considered, it is not possible to reach the point T_1, for between it and A, at T_2 (about 95·5° C.), the rhombic crystals change to monoclinic. T_2 is a triple point between two solids and vapour. From it there proceed the two curves T_2T_4 and $T_2'T_3$: the latter is the vapour pressure curve of monoclinic sulphur: the former gives the equilibria between the two solid forms, and the fact that it slopes away from the pressure axis shows that when rhombic changes to monoclinic there is an increase in volume. Increase in pressure is thus unfavourable to the change in this direction and a higher temperature is necessary to bring it about.

At T_3 (120° C.) monoclinic sulphur melts. T_3 is the triple point where solid, liquid and vapour coexist. T_3B is a normal vapour-pressure curve of a liquid and will end at a critical point. T_3T_4 is a solid-liquid curve similar to that of ice-water, with the difference that it slopes away from the pressure axis, monoclinic sulphur being denser than liquid sulphur. The slope of T_3T_4 away from the pressure axis is less than that of $T_2'T_4$ and the two curves therefore meet at a point T_4 (151° C. and 1,288 atmospheres pressure, and therefore much higher than shown in the diagram). Here three phases, two solid and one liquid, coexist. Beyond it the curve T_4C is that of the two-phase system rhombic sulphur and liquid, and from its slope it is apparent that this solid is also specifically heavier than the liquid.

The region in which monoclinic sulphur may exist is bounded by the three curves T_2T_3, T_3T_4 and T_4T_2. The

regions of existence of the remaining phases are as shown in the figure.

It is clear that the curves for the two-phase systems $S_1 - S_2$ and $S_2 - L$, though both sloping away from the pressure axis towards T_4, might be at such an angle that they would continuously diverge with increase of pressure instead of meeting at a triple point for $S_1 - S_2 - L$: or they might slope, the one towards, and the other from,

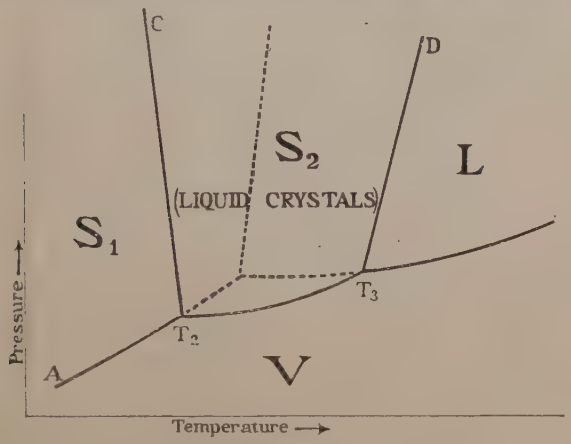


FIGURE 8.

the axis. In the latter case the diagram would take the form of Figure 8.

In such a case, unless the directions of T_2C and T_3D change at higher pressures, it is not possible for the three phases S_1, S_2 and L ever to coexist, or for a stable two-phase system $S_1 - L$ to be realized.

One component giving S, liquid crystals, L and V. An instance somewhat similar, and which will serve as an example of a one-component system in which two liquid phases (one of which is not isotropic) as well as the solid

and vapour are found, is that of p-azoxyanisol. The field S_2 is in this case that of the so-called 'liquid crystals' (a term much more justifiable than 'crystalline liquid', which is occasionally used); and the curve T_2C slopes like T_3D away from the pressure axis, but at a smaller angle. Hence here too there is the probability that the solid and (true or isotropic) liquid fields never become contiguous, or that solid p-azoxyanisol and its clear liquid form are unable to exist stably together.

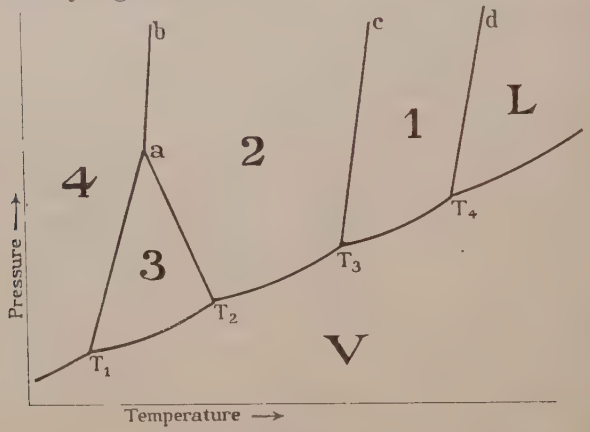


FIGURE 9.

One component giving several solids. As a last example of a system of one component which may exist in several phases, that of ammonium nitrate, represented in Figure 9, may be quoted.

Four different solid phases numbered 1, 2, 3 and 4, respectively, are possible according to conditions of temperature and pressure, and the system is of especial interest in showing the existence of a triple point (a) where the three phases are all solid. T_1, T_2, T_3 and T_4 are all triple points: at each of the first three two solids and a gas are in

equilibrium: in the last, liquid, solid and gas. The directions of the curves T_1a and T_2a were established by experiments going to 250 atmospheres, and on the basis of these Roozeboom predicted that there would be a triple point (with three solids in equilibrium) at about 69° C. and 1,170 atmospheres. Actually, Tammann found it later to be at 64·2° C. and 930 atmospheres. From it another curve ab, also verified by Tammann, gives the equilibria between the two solids numbered 2 and 4. The slopes of T_3c and T_4d make it probable that no solid but that numbered 1 can ever exist in stable equilibrium with liquid ammonium nitrate.

Unstable systems. So far attention has been directed only to the stable conditions of one-component systems. These are the conditions where, in thermodynamic terms, entropy is a maximum, or thermodynamic potential or internal energy a minimum, according to the particular type of the system. (See Chapter VII.) But it is often found that systems may exist in unstable equilibrium, the necessary condition being complete absence of the phase or phases of greater stability. Such cases are to be distinguished from those of merely apparent equilibrium where conditions of temperature are such that the rate of change from unstable to stable forms is infinitesimal in the presence of the latter.

It is unnecessary to discuss such cases in any detail, but two terms used in connexion with them must be mentioned. These terms serve to distinguish two types of system where a component is capable of existing in more forms than one.

Enantiotropy. If each form be stable over some definite range of temperature and pressure conditions, and there be therefore some condition at which the two coexist in stable equilibrium, the phenomenon is known as enantiotropy

(Gk. *ἐναντίος*, opposite; *τροπή*, turn), and the component is said to be enantiotropic. An example is given by sulphur and represented in Figure 7.

Monotropy. If, however, one of the forms be always stable, the other unstable, however pressure and temperature may vary, the phenomenon is termed monotropy (Gk. *μόνος*, single), and the substance is called monotropic. Figure 10 illustrates monotropy.

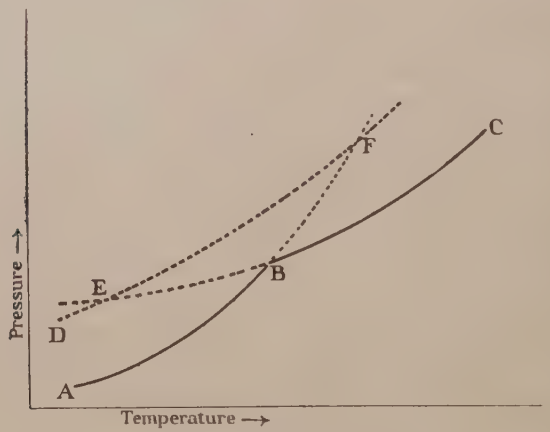


FIGURE 10.

AB is the vapour pressure curve of the stable solid form, *BC* of the liquid. *DEF* is the curve of the unstable solid form. It lies above *AB* and does not at any point cut it. The two forms cannot anywhere exist in stable equilibrium. A melting-point of the second is possible at *E*, and a transition point with the first form at *F*, but in both cases the systems are labile or unstable, and at equilibrium change to solid and liquid respectively.

Any one-component system may now be interpreted by reference to the typical cases which have been discussed.

CHAPTER IV

TWO-COMPONENT SYSTEMS

General. The introduction of a second component adds very much to the possible complication of heterogeneous equilibria. The maximum number of phases which may coexist is four, a system containing these being invariant. The apparently possible complexity is, however, not realized in practice. Thus, since all gases are completely miscible with one another, there is never more than one vapour phase; and no case is known where more than two liquid phases coexist, though there is not any reason on theoretical grounds to suppose the coexistence of three or even four liquids to be impossible; but the number of solids (single components or compounds of them) in equilibrium may reach the maximum of four.

In a univariant system there will be three phases; in a bivariant, two; and in a tervariant, one. Nothing is gained by taking account at first of all possible complexities: a very satisfactory idea of the relationships in two-component systems may be obtained from a consideration to which certain limitations are attached. It is proposed, therefore, to take as a basis for discussion a general case in which only a single phase may exist in the liquid as in the gaseous state, and where the solids may be only the single pure components.* To pass from this relatively simple case to others where more liquid phases and where either crystalline modifications of components or compounds or mixed crystals may appear, is not a matter of great difficulty.

* Subject to the qualification laid down in the Preface, p. 10.

The 3-dimensional p–T–c model. Graphical representation in three dimensions is necessary, and the most suitable method is by means of rectangular co-ordinates. Along two of them (*AC* and *BD* in Figure 11) pressure and temperature, respectively, are plotted; while along the third, *AB*, composition is given in fractions or percentages of the two components. Molar fractions or molar percentages are most satisfactory from the more usual points of view, though percentages by weight are often preferred. This is departing from the representation of specific volume

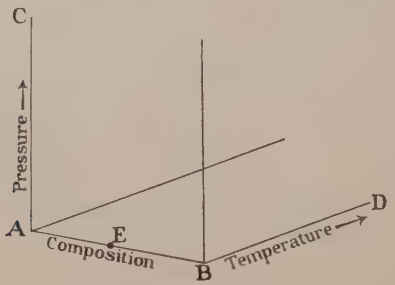


FIGURE 11.

adopted in the preceding chapter, but obviously it amounts to the same thing in that from a knowledge of the density of any phase the amount of each component in unit volume may immediately be deduced.

The point *A* corresponds with pure (or 100 per cent.) first component *A*; *B* with pure second component *B*. A point *E* would represent a system of which the fraction *EB/AB* would be component *A* and *EA/AB* component *B*.

This method of plotting has been adopted in Figure 12, which will now be examined in some detail. The figure is taken from Bakhuis Roozeboom's book, *Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre*, vol. ii (Vieweg und Sohn, Braunschweig). It should be kept in

view throughout practically the whole of this discussion of two-component systems.

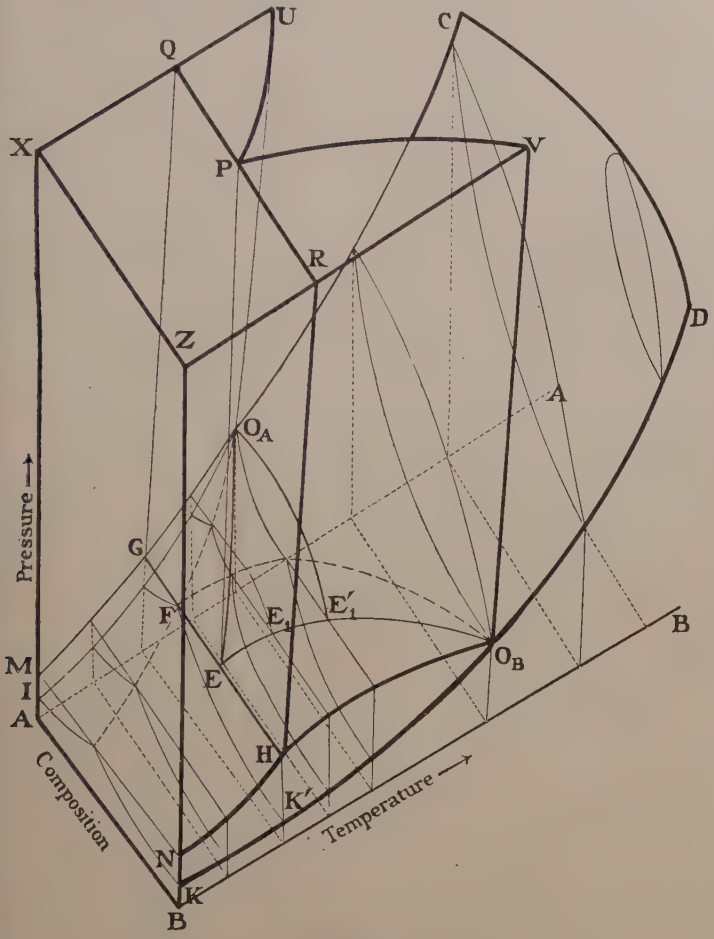


FIGURE 12.

Section showing phase regions. An isobaric section across the upper portion of the model at right angles to the pres-

sure-composition plane will give a preliminary general idea of the division of space between the phases. Such a section is represented in Figure 13 and shows the progress of change from solid ($S_A + S_B$) at low temperatures through liquid (L) at intermediate to vapour (V) at high temperatures.

Between these single-state (though, in the case of the solid, not single-phase) regions there come heterogeneous areas where solid and liquid, or liquid and vapour, coexist. A system, for example, of the mean composition represented by a point a will not exist stably as a single phase, but will separate into solid and liquid. The solid will be pure A, and the fraction ac/bc of the total complex will be present as such. The remainder, ab/bc, will be a liquid of the composition c. Similarly, of a complex represented at d, the fraction df/ef will be a liquid of composition e, and the fraction ed/ef a vapour of composition f.

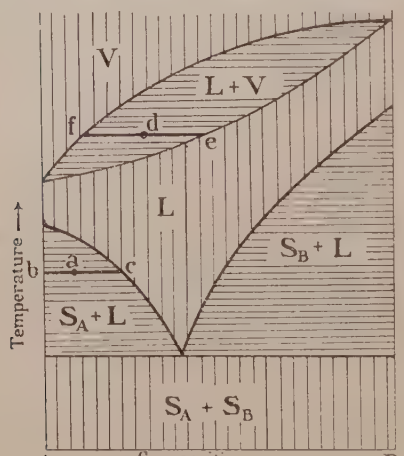


FIGURE 13.

At the pressure at which this section has been made, the three regions of solid, liquid and gas do not touch at any point. Only single-phase or two-phase systems are possible. The pressure is taken to be greater than the vapour pressure of the solid at any temperature at which the latter can exist: or, in other words, the pressure selected is too great to permit vapour to be formed from

a solid. But, naturally, at smaller pressures this relation may be reversed, so that in the lower part of Figure 12 a section would show a much less simple division, new heterogeneous equilibria becoming possible.

The liquid-vapour region $O_A C D O_B$. The systems at higher pressures will first be considered, beginning at the higher temperatures. At sufficiently high temperature, gas alone may exist. With fall of temperature liquid appears, and, provided the pressure be high enough, gas may disappear.

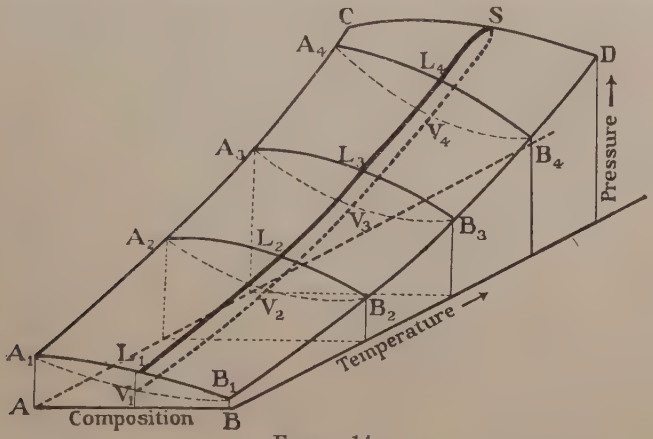


FIGURE 14.

The general relations are shown in the portion $O_A C D O_B$ of Figure 12, reproduced by itself in Figure 14.

The curve $A_1 C$ gives the vapour pressures at various temperatures of the pure liquid component A: $B_1 D$ those of the pure component B. For any given temperature the points A_1, B_1, &c., correspond, and are joined respectively by two curves $A_1 L_1 B_1$, $A_1 V_1 B_1$, &c., of which the upper gives compositions and pressures of the liquid containing both components, and the lower of the vapour in equilibrium with it. In the solid model formed from an infinite

number of such isotherms there are therefore two surfaces which may be called liquid and vapour surfaces, respectively, joining together along the limiting lines A_1C and B_1D, and also along the line CD, the significance of which will be discussed later.

Ideal isothermal (p-c) *sections of* O_ACDO_B. According to the natures of the components the forms of the isotherms $A_1L_1B_1V_1A_1$, &c., differ considerably. It is easy to deduce their courses for an ideal system, that is, for one in which Raoult's Law connecting partial pressures and molecular concentrations holds for the liquid, and in which the ideal gas laws hold for the vapour. In Figure 15, P_A is the vapour pressure of pure liquid component A at a given temperature, and P_B that of pure B. Any point c corresponds with a composition x of A and $1-x$ of B, best expressed in this case in gramme-molecules.

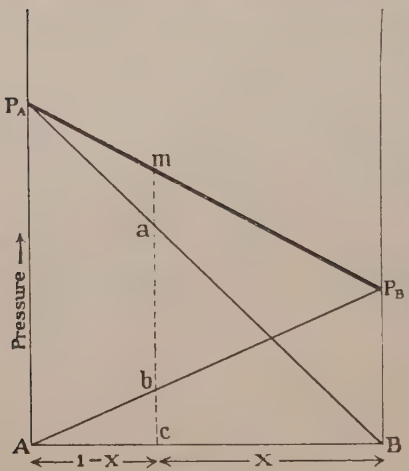


FIGURE 15.

Raoult's Law may conveniently be put in the form that the partial pressure of either constituent in a mixture is equal to the product of its vapour pressure when pure and its fractional molecular concentration in the mixture.

It follows that for a composition c the partial pressure of A will be $x \,.\, P_A$, which is equal to ca, where a is the intersection of a vertical line from c with the straight line

$P_A B$. Hence $P_A B$ gives the partial pressures of A in mixtures limited at the one end by pure A and at the other end by pure B. Similarly, AP_B gives the partial pressures of pure B in all these mixtures. For the point c, the two pressures are ca and cb; the sum is cm, where m is on the straight line $P_A P_B$. Thus, $P_A P_B$ is the curve (straight line) giving vapour pressures of all liquid mixtures from pure A to pure B.

The compositions of the corresponding vapour mixtures follow at once if the simple gas laws be expressed by saying that, at a given temperature, the molecular ratio of the constituents in the vapour is the ratio of their partial pressures. Hence, for a liquid mixture of composition c (Figure 15) the vapour in equilibrium will contain A to B in the proportion $ac : bc$, or say, $x_1 : 1-x_1$. We have then

$$\frac{x_1}{1-x_1} = \frac{ac}{bc} = \frac{xP_A}{(1-x)\,P_B} = \frac{x}{(1-x)} \times \frac{P_A}{P_B};$$

from which it follows that x_1 (vapour) will always differ from x (liquid) except in the single case where P_A happens to equal P_B. In that case both liquid and saturated vapour will be represented by a straight line $P_A P_B$ of constant pressure. In all other cases the compositions of liquid and vapour will differ. If P_A be greater than P_B, x_1 is greater than x, so that the vapour phase contains more than the liquid of the constituent with the higher vapour pressure: so, also, if P_B be greater than P_A. For any particular relation of P_A to P_B it is therefore possible at once to calculate the composition of vapour at pressure equilibrium with any liquid mixture. The form of the curve is hyperbolic and is represented by $P_A v P_B$ in Figure 16.

It flattens to a straight line and coincides with $P_A P_B$ when this line is horizontal; but as P_B differs more and

more from P_A it becomes further removed, as is shown for the cases B_1 and B_2. The vapour curve is, of course, symmetrical, but not with respect to the composition axis. Hence, the liquid differing most in composition from its vapour is not that which contains the components in equal molecular proportions, but one containing a greater fraction of the less volatile component. This may be seen in the lines vl and v_2l_2 in Figure 16.

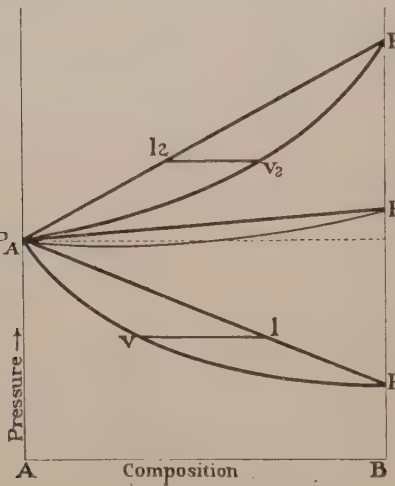


FIGURE 16.

Konowalow's Law. A general law enunciated by Konowalow concerning the relative positions of the liquid and vapour pressure-composition curves for binary mixtures is to the effect that the vapour phase, as compared with the liquid, always contains more of that component which, on addition to the liquid, raises its vapour pressure. Thus, it will be noted in Figure 16 that the vapour phase at v, say, at a given pressure, contains more of A than does the corresponding liquid phase l, and that A is the component the addition of which to l raises the pressure.

Usual types of isothermal section of O_ACDO_B. But since Raoult's Law does not hold except in the limiting cases where the proportion of the one constituent or the other is small, it follows that this ideal case of Figure 16 is not

found in practice unless the components have marked chemical similarity. The liquid curve usually deviates considerably from the straight line, lying sometimes below and sometimes above it. The simplest case is that represented in Figures 12 and 14, and from it, shown again in Figure 17, much information of practical value regarding the general behaviour of binary liquid mixtures may be deduced. Here the liquid curve runs continuously from P_A to P_B above the line $P_A P_B$; the vapour curve lies below it.

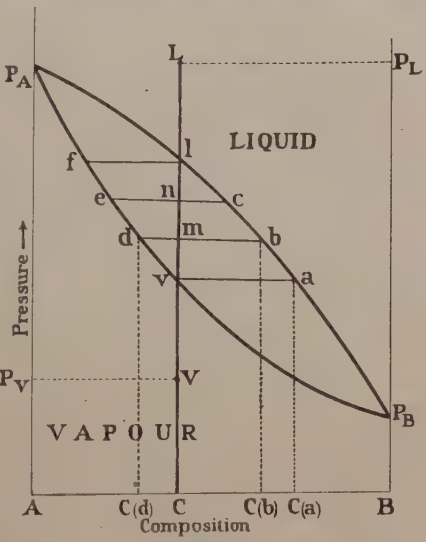


FIGURE 17.

Any mixture corresponding with a point in the area between the curves will separate into two phases, liquid and vapour. Above the liquid curve, only liquid exists; the pressure is too high to permit the formation of vapour. Below the vapour curve only vapour may exist.

Effect of isothermal change of pressure. If now any mixture, say that of composition and pressure given by V in Figure 17, be subjected to a steady increase of pressure from P_V to P_L, the alterations which the system undergoes may be read at once from the figure. Constancy of temperature is assumed, so that pressure changes in this and

any similar cases must be effected at a rate sufficiently slow to permit any necessary addition of heat from, or loss of heat to, surroundings to take place.

Up to, and including, the pressure corresponding with the point v, nothing happens to the system upon compression but change of volume. But an infinitesimal increase of pressure above v will result in the production of an infinitesimal amount of liquid phase of composition $C(a)$ corresponding with the point a on the liquid curve. The proportion of liquid will steadily increase with increase of pressure, and as its composition differs from that of the original vapour, the vapour composition must alter. At the point m there will be present liquid corresponding with b and vapour with d: and in the whole system, which may conveniently be termed a 'phase complex', the mean composition of which is C, there will be present the fraction md/bd of liquid of composition $C(b)$ and bm/bd of vapour of composition $C(d)$. The proportion of vapour steadily decreases. At n it is only nc/ce of the total. At l, on the liquid curve, it has reached zero. The system is once more a single phase of composition C, but now liquid. Further increase of pressure to L results merely in compression of this one phase. Reduction of pressure from L to V will bring about precisely the same changes in the reverse order.

Separation of components by isothermal evaporation (or condensation). In all this it has been assumed that the changes have occurred in a closed system without removal at any stage of any of the original mixture. But where separation of components is aimed at, as may be the case in laboratory or works practice, similar considerations may be applied. In practice, removal of vapour (or liquid) progressively formed would be made continuous, but, for

following the changes graphically, removal at regular intervals may be assumed.

If a liquid mixture of composition C and at pressure LC (in Figure 18) be subjected to decreasing pressure without removal of any phase, it will, at pressure VC, have been converted completely to vapour, and the liquid phase will have changed from composition L to an infinitely small quantity of composition l_2. No liquid nearer in composition to pure B can be obtained. If, however, the reduction of pressure be stopped at, say, a, midway between L and V, then liquid and vapour, l_1 and v_1, will be present in proportions readily calculated. If v_1 be now removed and l_1 subjected to a pressure decrease l_1b, it in turn will separate to l_2 and V. The amount of liquid l_2 will this time not be infinitesimal, but will be the finite fraction

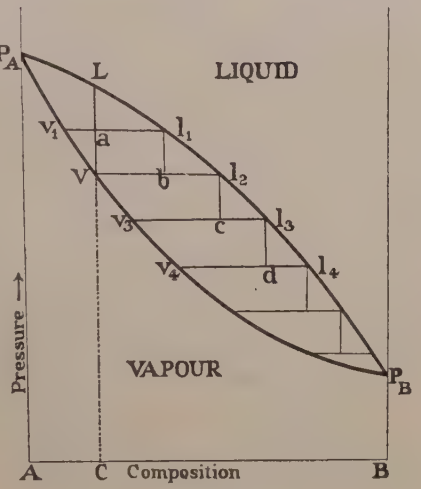


FIGURE 18.

$$\frac{av_1}{l_1v_1} \cdot \frac{bV}{l_2V}$$

of the original L: and it is clear that the more often, and hence the smaller the quantities in which, vapour is removed during the interval of pressure reduction LV, the greater will be the amount of liquid l_2 at the end. Then l_2 may be similarly partially vaporized to l_3 and v_3, and

v_3 removed: l_3 to l_4 and v_4, and v_4 removed: and so on. The amount of liquid is steadily decreasing as it approaches B in composition, and, of course, its amount is infinitesimal when it becomes pure B. A perfect separation of B in finite amount is thus impossible, but a separation of L into fractions may be effected, and these fractions will differ the more widely in composition:

(i) the smaller the volume of vapour formed in contact with liquid prior to its removal;

(ii) the more effectively the diffusion of successively produced vapours with one another, while still in the space above the liquid, is prevented;

(iii) the more rapidly vapour is removed.

Quite similar reasoning may be applied to the separation of components by fractional condensation of a vaporous mixture, with regular removal of liquid formed, leaving ultimately vapour of pure A.

Fractionation by isothermal evaporation or condensation of this kind is not so frequently applied in practice as isobaric evaporation or condensation. The latter will be considered in a similar way presently.

Other types of isothermal (p–c) *sections.* Although many cases of binary mixtures conform to the type of Figures 17 and 18, there are numerous others in which the liquid and vapour curves may not run steadily downwards or upwards from one pure component to the other; that is to say, in which the vapour pressures of mixtures may not all lie between the values for the respective components. In such cases the curves must pass through maximum or minimum points and take one or other of the forms shown in Figures 19 and 20.

A maximum is found on the side of the more volatile component A, a minimum on that of the less volatile B.

To each section P_AL and LP_B of the liquid curves in these figures must correspond a vapour section P_AV and VP_B, respectively. The generalization of Konowalow, mentioned above, which is based only on an assumption that the systems to which it is applied are in stable equilibrium, requires these to lie in the relative positions shown. The two curves touch at the maximum or minimum point as the case may be, and the systems are in accord with a general rule deduced by Gibbs to the effect that at a given temperature the vapour pressure attains a maximum or a minimum whenever the two phases become alike in composition.

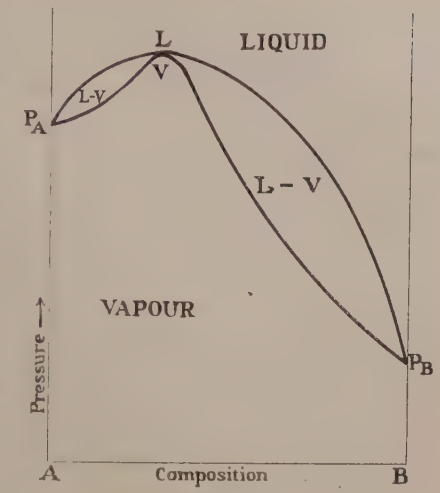


FIGURE 19.

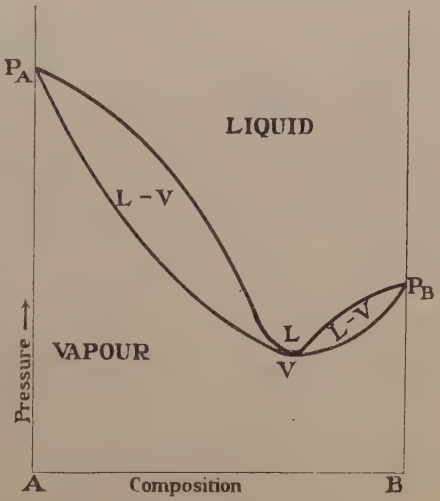


FIGURE 20.

If now there be applied to Figure 19 similar considerations to those already advanced for Figure 18 regarding isothermal distillation of liquid or condensation of vapour, with continuous separation of one phase as formed, it may readily be seen that for any mixture on the left of the maximum point the process will lead in the limit to pure liquid *A* and to vapour of the composition of the maximum point: on the right to pure liquid *B* and the same vapour. A separation into *A* and *B* is thus impossible. Liquid or vapour at the maximum point will evaporate or condense without change of composition just as a simple substance would.

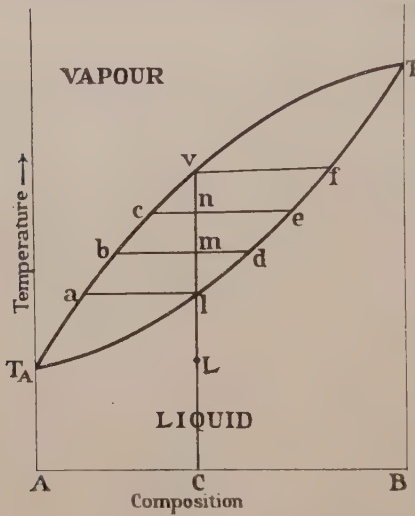


FIGURE 21.

Similarly in Figure 20 mixtures to the left of the minimum point may be fractionated in the limit to pure *A* vapour and liquid of the composition of the minimum point: mixtures on the right to pure *B* vapour and the same liquid. Again, *A* and *B* cannot, by isothermal evaporation or condensation, be obtained separately, as in the cases covered by Figure 18.

Isobaric (*T–c*) *sections of* O_ACDO_B. This discussion has proceeded from a consideration of isothermal sections of Figure 14. Two other types of section are possible, viz. those at constant pressure and those at constant composi-

tion. An isobaric section is given in Figure 21, and the curves are, in common phraseology, the boiling-point curves of binary mixtures. The case usually investigated is, of course, that of atmospheric pressure.

The space corresponding with conditions under which liquid alone may exist lies in the lower part of this section, and increase of temperature leads first to the heterogeneous area $T_A l T_B v T_A$, and then to the homogeneous vapour area.

The behaviour of a liquid mixture during isobaric distillation (or conversely of a vapour mixture during isobaric condensation) is readily predicted from the figure. If vapour be not removed as formed, the sequence of changes is the following:

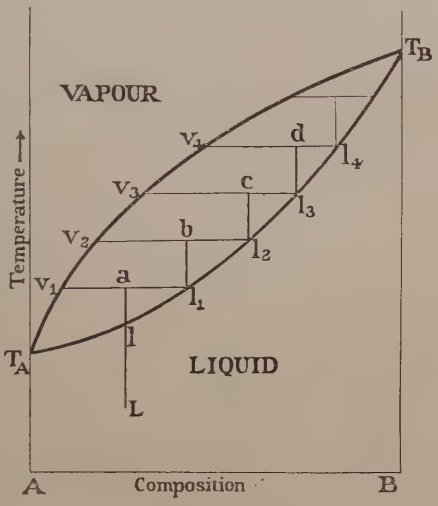


FIGURE 22.

A mixture of temperature and composition represented by L remains homogeneous till the temperature reaches that of l, when an infinitesimal amount of vapour of composition a is formed. With further heating the proportion of vapour steadily increases. At m the amounts of vapour and liquid are as $dm : mb$, the respective compositions being given by b and d. At n there is still more vapour, now of composition c as compared with liquid e. At v the liquid has just vanished, its last trace having the composi-

tion f. The system is now entirely vaporous and identical in composition with the original L. Vapour has thus varied between the composition limits a and v: liquid between l and f.

If, however, the vapour be steadily removed as formed, the sequence of changes may be read from Figure 22.

The liquid L remains homogeneous until at l vapour begins to form. If the first removal of vapour, v_1, be effected when the temperature corresponds with a, a liquid l_1 remains. This on further rise of temperature, $l_1 b$, gives liquid l_2 and vapour v_2; l_2 at c gives l_3 and v_3; and so on. The amount of liquid of composition and temperature corresponding with l_4 is

$$\frac{a\,v_1}{v_1 l_1} \times \frac{b\,v_2}{v_2 l_2} \times \frac{c\,v_3}{v_3 l_3} \times \frac{d\,v_4}{v_4 l_4}$$

of the original quantity. The case is very like that of isothermal evaporation discussed in connexion with Figure 18, and similar conditions determine the amount of residual liquid obtainable for a given rise of temperature.

The types of isobaric sections for the cases when the isotherms are similar to Figures 19 and 20 are readily drawn, and the course of distillation or condensation at fixed pressure, with or without removal of one phase as formed, does not present anything new.

Constant composition sections (p–T) *of* $O_A CDO_B$. There remain now the sections of Figure 14 at constant composition, one of which is shown by the curve

$$L_1 L_2 L_3 L_4 S V_4 V_3 V_2 V_1.$$

The co-ordinates here are temperature and pressure, and part of the curve is reproduced in Figure 23 as LSV.

The distance LV between the curves on the vertical line for any particular temperature gives the difference in pressure which results from isothermal vaporization or condensation. At pressure P_L the mixture is entirely liquid: at P_V en-

tirely vaporous. At a certain point S the two curves merge into one another. This holds for all mixtures, and the series of points gives the line *CSD* of Figure 14 shown as a projection in Figure 23. The phenomenon at each point is similar to that at the critical point of a simple liquid: the end points, C and D, of the line are, in fact, the critical points of the individual components A and B. Hence the name 'critical curve' is usually given to *CSD*. While it is not possible fully to discuss this curve here, one matter of contrast between the points of the critical curve of binary mixtures and the single critical point of a pure liquid should be mentioned. In the latter case the point is at the highest pressure and the highest temperature at which a two-phase system can exist: but with a mixture, the highest pressure and highest temperature of coexistence of two phases are not necessarily the values of these co-ordinates at the point where liquid and vapour phases merge into one another. Thus, in Figure 23, P is the point of highest pressure and T of temperature, while S is the critical point.

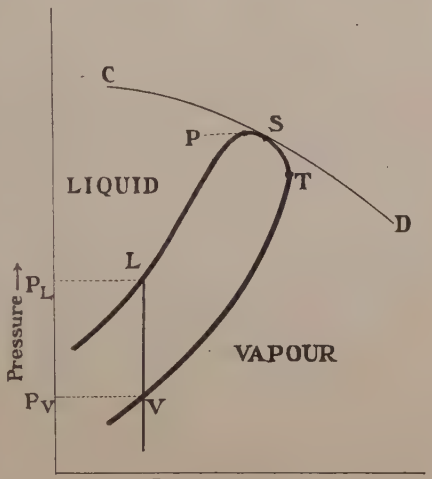


FIGURE 23.

There are other possibilities, too, and one of them is shown in Figure 24. A mixture subjected to the isothermal

changes indicated by the line *abc* will pass, in a case like this, with increasing pressure from a single vaporous phase to a liquid-vapour system, the liquid phase first appearing at *b*. At *c* it will become wholly vaporous again, and above that no pressure will liquefy the vapour. For fuller discussion of 'retrograde phenomena' of this kind, the original papers of Duhem (*Journ. Phys. Chem.*, 1897, **1**, 273 and 1901, **5**, 91), Kuenen (*Zeit. phys. Chem.*, 1893, **11**, 38 and 1897, **24**, 667) and van der Waals should be consulted.

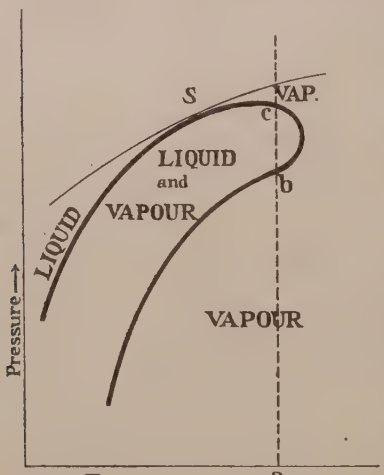


FIGURE 24.

Provided that no new phases appear, the two-surface model of Figure 14 will presumably extend continuously to absolute zero of temperature and to zero vapour pressure. But the formation of a solid phase is the usual result of passage to lower temperatures, and under conditions represented by points on the curves O_AE and O_BE of Figure 12 new equilibria enter. Before considering these, however, the case represented by the upper left-hand portion of Figure 12, shown already in section in the lower part of Figure 13, will be discussed.

Isobaric sections (T–c) such as XUPVZ of Figure 12. Here only solid and liquid phases enter. Pressures are too high and temperatures too low for a vapour phase to exist.

The number of investigated cases included in this general type is considerable, and from some practical points of view it is the most important portion of the two-component model.

As indicated in Figure 12, the effect of pressure on these liquid-solid or solid-solid systems is comparatively slight, and usually little change in the isobaric sections is to be noticed over a considerable range of pressure. In Figure 25 is given such a section, in which temperature and composition, respectively, are represented along the axes. The lower limit will be absolute zero. The upper limits, where vapour appears, have already been shown in Figure 13.

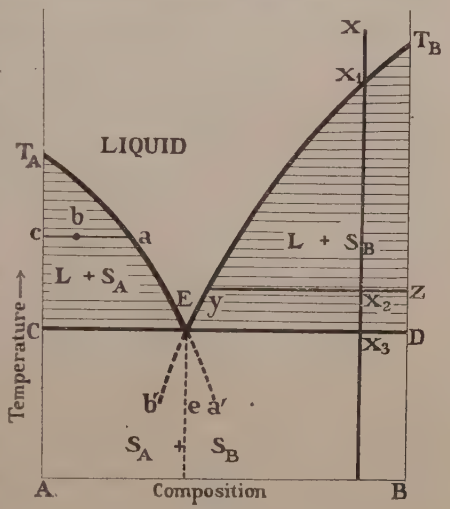


FIGURE 25.

T_A is the melting-point of pure A under the selected pressure: T_B of pure B. The addition of a small amount of the one to the pure melt of the other will lower the temperature of equilibrium between solid and liquid. In accordance with the laws of dilute solutions, this lowering will be proportionate to the number of molecules added, and if the compositions along the axis AB be expressed in molecular fractions, the curves for lowering of melting-points will be straight lines. As, however, these simple

laws hold only for dilute solutions, the curves from T_A and T_B usually show an approximation to straightness over only the first parts of their courses.

Along T_AE are represented the liquids of steadily increasing concentration in B, which are in equilibrium with solid A,* represented along the vertical line T_AC. Any mixture of components, or phase complex, of mean composition corresponding with a point, such as b, within the area T_ACE will resolve itself into solid A (point c) and a solution on T_AE, such as a, where a, b and c lie on a horizontal straight line. Of the total complex, ab/ac will be solid A, and bc/ac will be liquid.

The number of degrees of freedom possessed by any two-component system in two phases is two, but one of these having been exercised in the present case in an arbitrary selection of pressure, such a system has become univariant. Any line like abc may thus be termed a univariant conjugation line, and the area T_ACE a univariant area.

Precisely similar considerations may be applied to the area T_BDE and its bounding and conjugation lines.

Eutectic temperature and composition. At E equality in concentration is reached in the two series of liquids. Here, therefore, solid A, solid B and solution exist in equilibrium. Three phases of two components constitute a univariant system, which, under a selected pressure, becomes invariant.

The invariant point E is obviously at the lowest temperature at which, under a given pressure, a liquid phase can

* Again the student may be reminded that the solids in equilibrium with successive liquids along T_AE cannot be identical, that is, perfectly pure A, though in the case under consideration differences in composition from pure A may be negligibly small. It has already been stated in the Preface (p. 10) that for reasons of simplicity in presentation the exact compositions of solids will not be taken into account at this stage. See also the opening part of Chapter VIII.

exist, and its composition is such that it can coexist with both components. This amounts to saying that the particular proportion of solid components corresponding with E is one that melts completely at a lower temperature than any other. Hence it has become customary to call it the 'eutectic (Gk. εὔτηκτος, easily-melting) mixture', or more briefly, the 'eutectic', and the point E the 'eutectic point'. In the earliest cases investigated, the components were, respectively, water and some salt or other, and because the eutectic temperatures where ice and solid salt coexisted with a certain solution were always below, and often many degrees below, the freezing-point on the thermometric scale, the name 'cryohydric temperature' (Gk. κρύος, frost; ὕδωρ, water) came into use. There is no particular reason, other than that of historical interest, for retaining such a term, and it might be as well to abandon it altogether. A eutectic point, in all these binary systems, varies slightly, though only slightly, with pressure, and measurements are customarily made under a total pressure equal to one atmosphere.

Returning to Figure 25, the horizontal line CD, an invariant conjugation line connecting the compositions C, E, D of the three coexisting phases, is the lower boundary of both the liquid-solid univariant areas T_ACE and T_BDE. Below it only solids can exist. If, then, the eutectic solution E be cooled, there will separate from it solid A and B side by side. That this must be so will be evident if one supposes E supercooled to e, for a solution e is supersaturated with A and B relatively to the unstable prolongations of T_AE to a' and T_BE to b', respectively. The mean composition of the two-phase solid will be the same as that of the liquid, so that the freezing-point phenomenon recalls that of a single component. Since,

however, the composition of the eutectic varies (however slightly) with pressure, the constancy of the freezing-point at a given pressure is no more evidence of the presence of a single phase than was the identity of composition of liquid and vapour during isothermal evaporation at the point L in Figure 19. The proportions of A and B in the solidified eutectic mixture will obviously be ED/CD and EC/CD, respectively.

Changes with altering temperature. If now any liquid mixture, say that of the point x, be cooled, the changes in it may be quantitatively predicted from Figure 25. Until the temperature reaches that of x_1, on the curve T_BE, cooling does not bring about any phase reaction. Below x_1, however, separation of solid B begins, the residual liquid becoming therefore relatively richer in A and moving along the curve x_1E. At the temperature of, say, x_2, the fraction x_2y/yz of the original mixture will be present as solid B (z), and the rest as solution of composition y, the points y, x_2 and z lying on the horizontal conjugation line. At x_3, on CD, the fraction that is liquid, x_3D/ED, has decreased still further, and this liquid is now of eutectic composition. On further cooling, the latter will solidify as a whole. These proportions then are those of B and eutectic solid, respectively, in the total solid. Since the eutectic is itself composed of A and B separating side by side, the total composition may also be expressed as Cx_3/CD of B and x_3D/CD of A. In the process of cooling from x, however, one may imagine crystals of B steadily growing, and at x_3 the eutectic mixture filling the interstices between them and then quickly freezing to a mixture of comparatively small crystals of A and B. Hence, there is some reason from a purely descriptive point of view for preferring to describe the solid in terms of the more sharply contrasted portions B and

eutectic solid, rather than in terms of A and B. In any text-book on metallography (for example, Desch, *Metallography*, Longmans, Green & Co.) will be found photographs of magnified polished solid surfaces of two-component alloys which illustrate this point.

Cooling below x_3 does not bring about any further changes in phase. The solid components remain together in the proportions formed at x_3. The area is thus one of the coexistence of two solid phases.

All such curves as T_AE and T_BE of Figure 25 lie upon the surfaces UO_AEP and VO_BEP of Figure 12, or their continuations upwards. These surfaces, then, separate the space in which liquid alone exists from those spaces in which solid may coexist with it.

Modifications due to formation of compounds. The relatively simple case of Figure 25 may become more complicated if the two components are able to unite to form one or more compounds. Where A and B are metals ever so many cases of the kind are known: so, too, where one is a solvent such as water and the other a salt. Indeed, the case of Figure 25, though frequent with metals, is not altogether usual with common solvents and solutes. T_AE is the freezing-point curve* of increasingly concentrated solutions: T_BE is the solubility curve* of the anhydrous solute. It is seldom that one finds a complete curve from the cryohydric or eutectic temperature to the melting-point T_B of solute. Figure 26 represents the chief features of the more usual systems.

T_AE is the freezing-point curve of solutions containing progressively increasing amounts of component B. At E,

* It is often convenient to use these familiar terms, though it is perfectly obvious that there is no difference in kind in the two curves, so that, from a pedantic point of view, the practice is unjustifiable.

a eutectic (cryohydric) point, it meets the curve CE, the liquids of which are in equilibrium with a solid compound of composition corresponding with the point C, say A_xB_y. At C the compositions of liquid and solid are identical, so that this is the melting-point of the compound. A perpendicular DC' through C will now cut off a portion $T_AAC'CD$ of the whole figure which is in every way similar to Figure 25. The two components are A and a compound containing this and B, instead of two quite distinct elements or compounds, A and B.

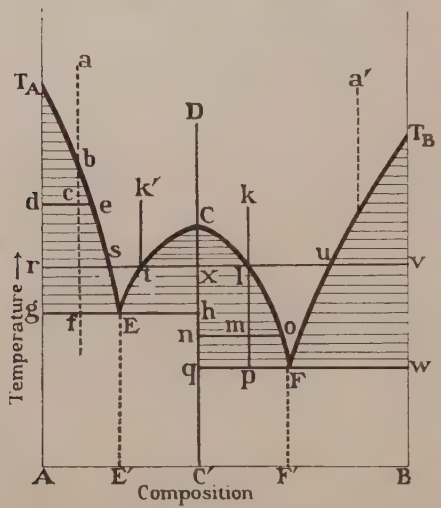


FIGURE 26.

Just as the freezing-point of A_xB_y is lowered from C by the addition of A to the melt, so is it by the addition of B. Hence, on the other side of CD a curve CF is obtained which meets, at F, the second eutectic for the system, the curve T_BF for the liquids in equilibrium with solid B. The whole system is really nothing more than Figure 25 twice over. The curve EF which runs from the one part to the other is continuous, that is to say, there is no sudden change of direction at the maximum point C.

The division of the whole field into its various systems of phases will be readily apparent from the figure.

Changes with alteration of temperature. It follows from

what has been said that one is always able to read from such figures as 25 and 26 the way in which any mixture of the components will resolve itself into phases and the proportions between the phases. Such diagrams give precise, quantitative information about any possible binary mixture at any temperature, a fact which is not fully appreciated when, as is so often the case, attention is directed only to curves and their intersections and not to the equally important areas of which the curves are merely the boundaries.

By way of example, the behaviour of any mixture of A and B in such systems as those of Figure 26 may now be deduced. All mixtures represented by points above T_AECFT_B are completely liquid. The changes occurring on cooling depend upon the particular curve above which a point may lie. Any mixture such as that at a, lying above T_AE, remains liquid until it cools to the temperature of b on the curve T_AE. Here an infinitesimal amount of solid A separates. The amount steadily increases as the temperature falls, and at c the fraction ce/ed of the total will be present as solid A and cd/de as solution of the composition e, richer, of course, in B than the original a.

'*Thermometric arrests.*' If the cooling agent be constant throughout, it will be found that from a to b the rate of fall of temperature is greater than from b downwards. For, in accordance with the principle of Le Chatelier and Braun, the change in the system, beginning at b, is of a kind to counteract cooling; that is to say, it is an exothermic change, the heat set free being that commonly referred to as the latent heat of solidification of the separating component A. Hence, as compared with ab, bc shows a 'thermometric arrest' of cooling which continues until the point f is reached. Here, fE/Eg has solidified, and the rest of the original mixture, the fraction fg/Eg, is the eutectic

liquid of composition E. Any attempt to cool this liquid further results in its solidifying to a eutectic mixture, similar to that of E in Figure 25. In this case, however, the two phases of the eutectic are solid A and the solid compound A_xB_y of composition C; Eh/gh of the liquid going to the former, and Eg/gh to the latter. The total solid obtained may be represented in proportions of the original weight taken either as fg/gE of eutectic of the composition just quoted and fE/gE of solid A, or else as fh/gh of solid A and fg/gh of solid compound A_xB_y.

Since the eutectic liquid E solidifies as a whole, the phenomenon is different from that of the passage along the line bf, where there is a continuous adjustment of composition of the liquid phase. The case is, in fact, quite like that of the freezing-point of a pure substance. Any attempt to cool the mixture results, by separation of solid, in production of heat sufficient to annul the cooling and keep the temperature at that of E until all liquid has solidified. Hence, there is here a much more marked thermometric arrest than along bf under constant cooling agency.

In the many difficult investigations which have been carried out upon binary mixture of metals, rates of cooling ('thermal analysis') have been of great importance in determining equilibria. It is not possible here to go further into a practical question of this kind. Details will be found in Desch's *Metallography* (Longmans, Green & Co., London) or Giua's *Chemical Combination among Metals* (J. & A. Churchill).

The cooling of a mixture a' above FT_B is, of course very similar to that of a. A mixture k above CF (or, *mutatis mutandis*, k' above EC) will remain liquid to l when the solid compound A_xB_y will begin to separate. At m the fraction om/on will have solidified and mn/on will still be

liquid though now of composition *o*. At *p* the liquid will be the eutectic mixture *F*, and, on attempted further cooling, it will solidify without further change of composition to the two phases, compound and pure *B*. The proportions in the solid are, as before, at once calculable.

Region of solid phases. For the regions in which only solid phases exist, that is to say, below the boundary *gEhqFw*, the following summary holds:

In the area *AghC'*, *A* and A_xB_y exist side by side: in *AgEE'* the mixture may be regarded as one of *A* and eutectic of composition *E'*, and in *E'EhC'* as one of A_xB_y and eutectic. In *C'qwB*, similarly, *B* and A_xB_y exist together: in *C'qFF'* the solid may be considered as a mixture of A_xB_y and eutectic *F'*, and in *F'FwB* of eutectic and solid *B*.

Changes with alteration of composition. It is of interest, also, to make use of a diagram such as Figure 26 for predicting the changes which must occur when, at constant temperature, a system undergoes a steady alteration of composition; when, for example, pure *A* at a temperature corresponding with *r* receives continuous additions of *B* (or what would come to the same thing, when some mixture of *A* and *B* steadily loses *A* by, say, evaporation), passing through all possible compounds until the limit, pure *B*, is reached.

At first the pure *A* is solid, being the interval $T_A r$ below its melting-point. The addition of *B* causes partial liquefaction, the new liquid phase having the composition of *s*. The proportion of the total mixture which is liquid steadily increases until complex and *s* have the same composition, at which point *A* has vanished. Further additions of *B* dissolve, a liquid phase of changing composition from *s* to *t* alone being present. At *t*, however, solid again appears, this time the compound A_xB_y. The amount of it increases

with more B, the liquid remaining at t and decreasing in quantity until at x this phase disappears and there is present only pure solid compound. With more B, liquid l is formed and increases in quantity until the whole complex consists of it, A_xB_y having disappeared. From l to u is an interval of liquid solutions of increasing content in B, but at u, solid phase, the pure component B separates. Thence onwards addition of solid B has no effect; the solid simply accumulates. If, however, the relative amount of B be increased by withdrawal of A, B will continuously form and the liquid u diminish in amount to zero.

The alteration of composition has therefore resulted in passages from one solid phase A to a two-phase system of A and liquid, then to a one-phase system of liquid, to two-phase solid A_xB_y and a second liquid, one-phase solid A_xB_y, two-phase solid A_xB_y and another liquid, one-phase liquid, two-phase solid B and liquid and finally a single-phase system of pure B.

While all this deduction is quite logical, it is necessary to point out that from the practical point of view the realization is not necessarily easy. Thus the addition of solid B at temperature r to solid A at the same temperature will not invariably result in the immediate formation of the stable system solid A and liquid s. The rate of progress to equilibrium may be indefinitely slow, and only to be effected practically by passing first through other conditions: but the final equilibrium states must in all cases be those indicated.

Metastable melting-points of compounds. Only one other point remains to be mentioned in connexion with systems of this type. In Figure 26 the curve T_BF (solid B) meets the curve ECF (solid A_xB_y) beyond the maximum C. It is frequently found, however, that the equilibrium point

between A_xB_y and solid B is reached on the part EC below C; that is to say, the liquid with which the two solids may coexist is richer in A than the compound A_xB_y. Figure 27 shows such a case.

C is now a metastable or labile point. If pure solid A_xB_y be raised to the temperature C, it certainly forms solid and liquid, but when the new equilibrium is attained, the former (*bC/be* of the total) is pure B, not A_xB_y, and the latter (*Ce/be* of the total is of composition *b*. Pure solid A_xB_y can thus exist stably only in the presence of a liquid containing more A than it itself does; the point F is the poorest in A of such liquids.

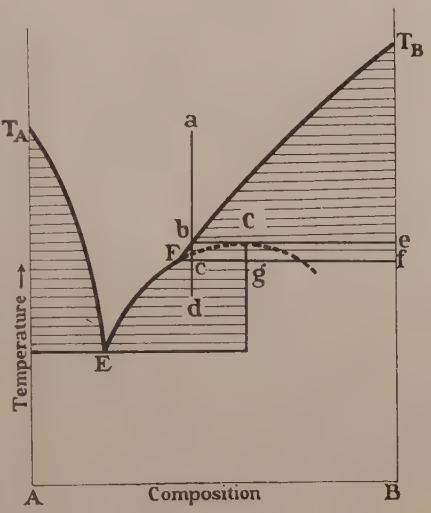


FIGURE 27.

As compared with the interpretation of Figure 26, that of Figure 27 offers little else that is new. A consideration of the changes occurring on cooling a liquid mixture at *a* will suffice to emphasize what differences there are. The single phase, liquid, persists until the temperature is that of *b*. Below this pure B separates, the liquid becoming relatively richer in A until it reaches the composition of F when cF/fF of the original mixture has separated as B. At F a new solid phase, the compound A_xB_y, appears, and any further attempt to cool the mixture will result in the

separated B redissolving, while more A_xB_y forms. So long as any solid B remains, the temperature cannot be changed. Since the attempt to cool the mixture results in solution of B and the separation of A_xB_y, it follows from Le Chatelier's theorem that the heat developed in the latter process must exceed the cooling consequent upon the former.

When all B has returned to solution, Fc/Fg of the system is present as solid A_xB_y, and cg/Fg as solution F. On further cooling, more compound separates and the solution ultimately reaches the eutectic point E at which A appears. The case thereafter is identical with that previously outlined in connexion with Figure 26.

One may express the differences between the cases of Figures 26 and 27 in another way by comparing the corresponding conjugation lines, qFw and Fgf, respectively. The relation between the phases whose compositions lie on the former is given by the equation

$$\text{Solid } A_xB_y\,(q) + \text{Solid } B\,(w) \rightleftarrows \text{Liquid } (F).$$

Between those lying along the latter it is

$$\text{Solid } A_xB_y \rightleftarrows \text{Liquid } (F) + \text{Solid } B\,(f).$$

The direction of reaction depends upon the direction of temperature alteration, the upper arrow in each case giving the change occurring with rise of temperature.

Transition points. Since at the point F in Figure 27 the change consists in the conversion of, or transition from, one solid to another, such a point is commonly termed a transition point to distinguish it from the eutectic point of Figure 26. There is one outstanding difference between the two which is implicit in the equations above. Increase of temperature at the transition point F gives liquid in equilibrium with solid B, the solid A_xB_y having disappeared: decrease gives liquid with solid A_xB_y, solid B

having diminished to zero. Thus liquids may exist above and below a transition point. On the other hand, increase of temperature at a eutectic point gives liquid with either solid B or solid A_xB_y: decrease gives solids only. The eutectic point, then, differs from the transition point in being the lowest temperature at which a liquid can exist.

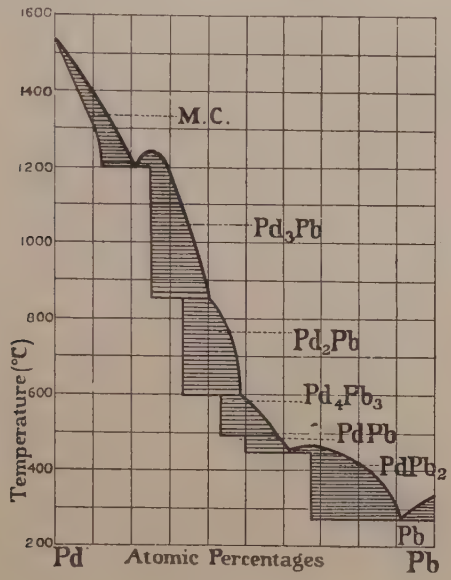


FIGURE 28.

Some actual examples. If now Figures 26 and 27 be understood, there will be no difficulty in interpreting such diagrams as are given in Figures 28 and 29. The former (taken from Giua, *Chemical Combination among Metals*, p. 234), for the binary system lead-palladium, is an excellent example of the relations found in investigations on alloys. The part marked M.C. is rather different from

any case so far discussed and its type will be referred to again in Chapter VIII.

Figure 29 is from the work of Roozeboom (*Zeit. phys. Chem.*, 1892, **10**, 477) on ferric chloride and water, and is typical of so-called 'solubility work' on binary systems of salt and solvent. These two cases are rather more complicated than the majority of their kind.

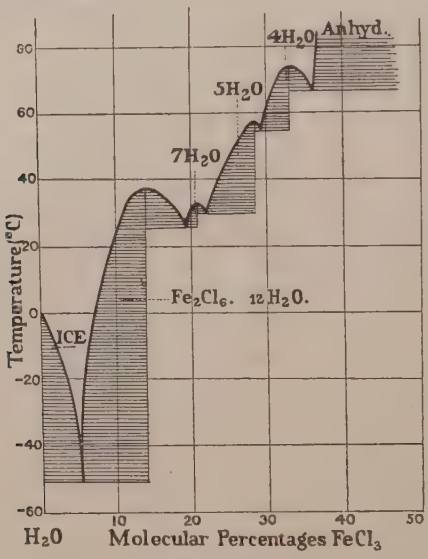


FIGURE 29.

The lower portion of Figure 12. There remains now for detailed consideration that portion of the typical space model which is shown in the lower part of Figure 12. Here pressures and temperatures may both be low and, in consequence, rather more complicated equilibria may occur. The most satisfactory way of grasping the significance of the model is to study it in successive isothermal sections. Much assistance in understanding its various divisions in

these lower parts will be obtained from the perspective sketches shown in Figures 30 and 31, which are taken in

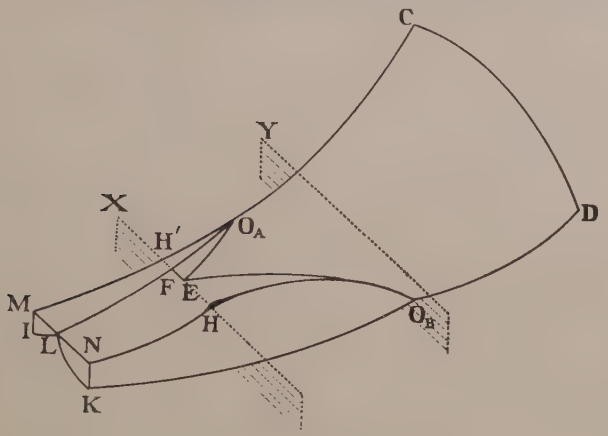


FIGURE 30

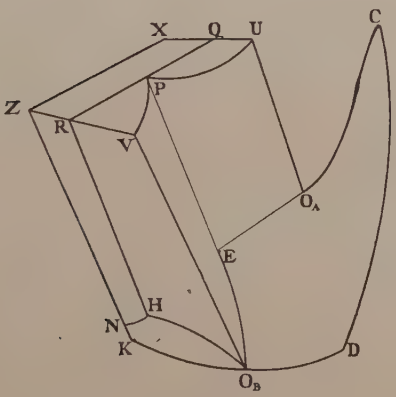


FIGURE 31.

outline directly from Roozeboom's *Die heterogenen Gleichgewichte*, vol. ii, and which should be examined in conjunction with Figure 12.

Successive isothermal (p–c) sections. Figure 32 gives a succession of isothermal sections illustrating the changes which occur when solid phases begin to appear as one passes to lower temperatures and pressures in the continuation of that portion of the model which is sketched in Figure 14. They are sections extending from I' to X in Figure 30.

It will be assumed as before that, at a given temperature, liquid component A has a higher vapour pressure than

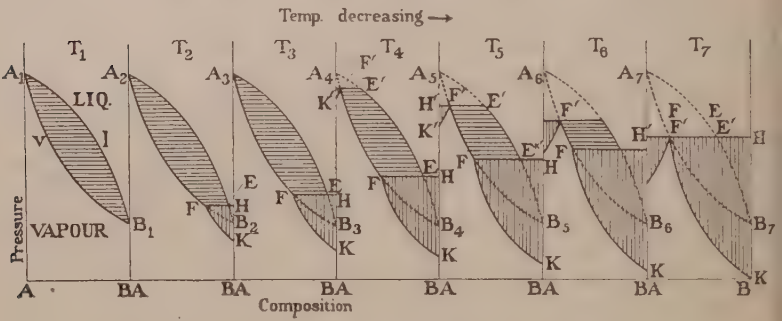


FIGURE 32.

liquid B. As a rule, though not invariably, it follows that B will solidify before A, and it will be supposed here that it does so. The general case is not altered if the reverse holds. No compounds between, or mixed crystals containing, the components will be taken into consideration. The principles involved in these cases are identical, but there is of course added complication in the graphical representation, and it is not considered worth while to undertake their detailed discussion.

Section T_1 of Figure 32 shows the bivariant system liquid-vapour, for a selected temperature, already discussed in connexion with Figure 17. A_1 is a point on the vapour-

pressure curve CO_A (Figure 12) of pure liquid A; B_1 on DO_B of pure liquid B. $A_1 l B_1$ gives compositions of liquid phases, and $A_1 v B_1$ of corresponding vapour phases.

As temperature falls, so on the whole will vapour pressure, but no attempt has been made to represent relative pressures in corresponding portions of the various sections in Figure 32. At a temperature O_B (Figure 12) it becomes possible for solid B to separate from its own melt. When, however, any A is present in the liquid, solid B cannot remain. The partial vapour pressure of liquid B is lowered by dissolved A, so that solid B in contact with a solution would inevitably dissolve. But if the temperature be lowered it becomes possible for B to exist with solution containing A: the case is illustrated by section T_2 of Figure 32. B_2 is here the vapour pressure of metastable liquid B. The pressure of the stable solid is therefore lower, say that of the point K. In the liquid and vapour phase equilibrium, now, the partial pressure of B steadily decreases from B_2 with addition of A, though of course the total pressure increases. It is therefore possible to find a point at which liquid E and vapour F are in equilibrium at a total pressure to which B contributes a value equal to BK: or, in other words, there is here a point at which solid B is in equilibrium with vapour and liquid both containing A and B. The portions EB_2 and FB_2 of the liquid and vapour curves are no longer stable systems in presence of solid B, since the partial pressure of the latter in them is always greater than BK. The curve FK gives the concentration of the vapour phase in equilibrium with solid B, and, so long as the proportion of B is greater than corresponds with F, no liquid phase can be formed.

At a still lower temperature, section T_3, the phenomena remain of similar kind, but the difference KB_3 is increased,

and F and E are further up their respective curves. The remaining sections show the steady increase of the region FKH of coexistence of solid and vapour, without liquid. At some temperature, a little below that of section T_3, the melting-point O_A (Figure 12) of pure A will be reached. In section T_4, AK' is the vapour pressure of solid A, and AA_4 that of its metastable liquid. As addition of B will lower the latter, a value corresponding with E' on the liquid curve and F' on the vapour curve must ultimately be reached at which the partial pressure of B in the mixture is equal to AK'. We have thus much the same case as with B, except that the total vapour pressure at which solid, liquid and vapour coexist clearly falls between that of pure solid, AK', and metastable pure liquid, AA_4. In the other case it was above both.

Sections T_5 and T_6 show further advances in these changes. The regions in which solid A and vapour, and solid B and vapour, coexist are steadily increasing. That in which liquid and vapour coexist, without solid, is gradually decreasing. Section T_7 shows the temperature at which the latter just disappears. F and F' coincide : so do E and E'. At the pressure $H'F'E'H$ and temperature T_7, solid A (H'), solid B (H), liquid (E') and vapour (F') exist together. It is the one four-phase or invariant system possible with two components which show only the relations assumed in Figure 12.

If now these and all intermediate sections be put together, they will be seen to form the portion of Figure 12 running from a little above O_B (and hence O_A) so far as the temperature corresponding with the line $GFEH$, but bounded above by the surfaces O_AEG and O_BEH. It is better visualized from Figure 30 as the portion cut off between the levels of the planes Y and X. The appearance

from below of the under portion of Figure 30, the line of vision being parallel to the pressure axis, is diagrammatically represented in Figure 33. The directions of rise of the three curved surfaces seen are indicated by arrows. A line at or about the level KK' would correspond with the isotherm T_6 of Figure 32.

The close examination and comparison of Figures 12, 30, 31 and 33 at this stage will amply repay the student. Sufficient description has been given to enable any one to tell what phases exist at particular points, on particular lines and surfaces, and in particular volumes, and hence to appreciate the precise types of system represented.

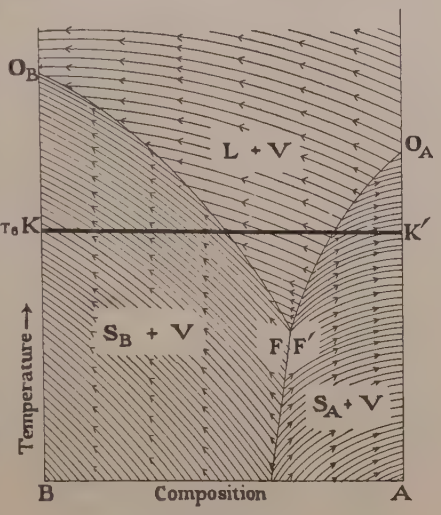


FIGURE 33.

More complete isotherms. To complete the whole discussion and bring more into line its different divisions, a few rather more complete isotherms will now be given, embracing the region covered by the isobars of the type of Figure 25. The form of these will depend upon the way in which pressure affects the temperatures of equilibrium in systems containing solid and liquid bounded by the melting-points of the components on either hand and the eutectic in between. This comes to the same thing as saying that the form of the isotherms will depend upon the slopes of

the curves O_AU, O_BV and EP, respectively, in Figure 12. The slopes depend, of course, upon the relative specific volumes of liquid and solid phases of components or eutectic, as the case may be. If, as in the case of water, fusion occurs with contraction, then with increase of pressure the curves will slope towards lower temperatures. It will be assumed, however, that the more general case of expansion on fusion holds both for individual components and eutectic, so that the curves O_AU, O_BV and EP will be assumed to pass towards higher temperatures as pressure increases.

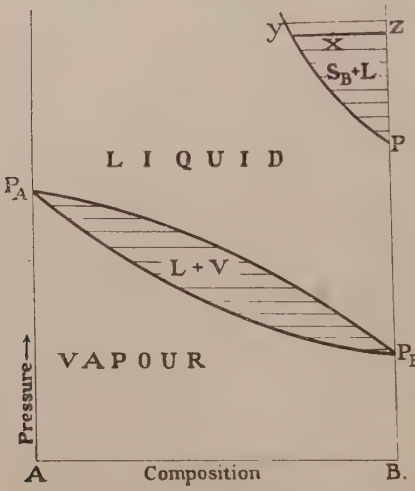


FIGURE 34.

Isothermal section just above O_B. Figure 34 gives an isothermal section taken a little above the temperature O_B. The sections should be studied along with the models, Figures 12, 30 and 31.

At a sufficiently high pressure, P, liquid can be compressed to solid. The higher the pressure the more solid is formed. As the solid is pure B, the residual liquid becomes relatively richer in A and hence less readily separates B. A succession of equilibria is brought about. With a mixture of composition and pressure corresponding with x, for example, xy/yz of it solidifies to B : xz/yz forms

liquid of the composition y. The rest of the figure offers nothing new.

At lower temperatures P and P_B approach and at O_B (the melting-point under ordinary pressure) they coincide.

Section between O_A and O_B. At a temperature between O_A and O_B the vertical section is that shown in Figure 35.

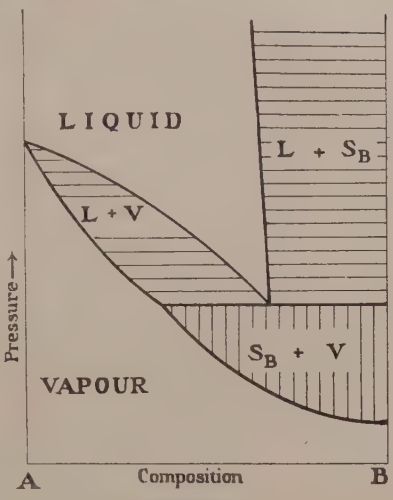


FIGURE 35.

The notation in the figure sufficiently explains the division and limits of the different phases. There may here appear on the A side of the diagram an area $S_A + L$ (not shown) similar to $S_B + L$ in Figure 34.

Section below O_A. Below the temperature O_A, solid A can exist, and between O_A and the eutectic temperature the section is of the form of Figure 36.

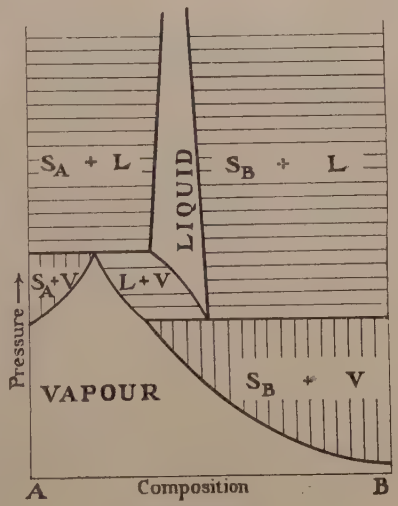


FIGURE 36.

Still nearer the eutectic temperature, it may be that the liquid region becomes totally enclosed and the section changes to that of Figure 37, cutting through the line EP at a point p.

At all pressures above p, mixtures of A and B are entirely solid, being two-phase and consisting of crystals of the

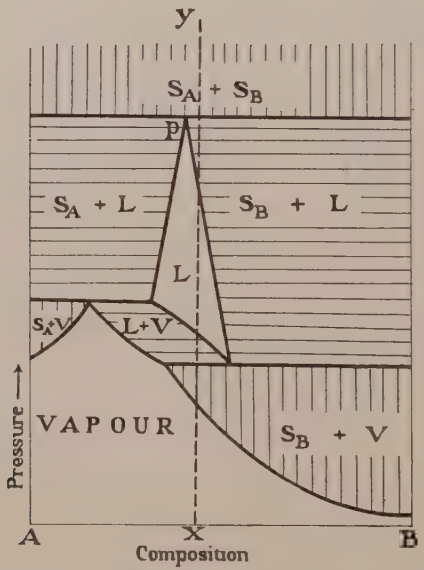


FIGURE 37.

components side by side as already discussed in connexion with Figure 25.

With decrease of temperature, the regions denoted by $S_A + L$, $S_B + L$, $L + V$ and L steadily diminish until at or below the invariant point E the type of isothermal section is that of Figure 38, the interpretation of which requires no further statement.

These figures, 34–38, will be seen to include the sections

in Figure 32, but to show in addition those regions in which the vapour phase does not appear.

If the slopes of the curves $O_A U$, $O_B V$ and EP be other than as assumed, the consequential modifications in these diagrams are readily made. It will serve as a good exercise for a student to sketch the isotherms for such cases and also to work out the changes which occur with changing

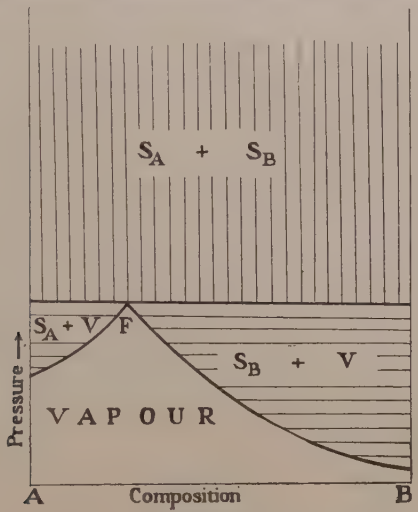


FIGURE 38.

pressure in a system of, say, composition x at the temperature of Figure 37.

There are, of course, numerous points connected with two-component systems which have been omitted from this discussion, which has, however, traversed the chief characteristics. The whole subject has been worked out very fully by Roozeboom and Schreinemakers, and any one wishing for further detail will be well advised to study the original works of these distinguished investigators and their pupils.

CHAPTER V

THREE-COMPONENT SYSTEMS

General. With the addition of a third component, the sum of the degrees of freedom possessed by any system and the number of phases present in it becomes equal to five. The greatest number of phases that may be present in general equilibrium is therefore five, being one more than in the corresponding invariant system of two components.

Only one gaseous phase is possible: the remainder may be all solid or all liquid (though no actual case is known where all are liquid), or some may be solid and the rest liquid. Univariant systems contain four phases; bivariant, three; tervariant, two; quadrivariant, one.

The maximum number of degrees of freedom in the simplest possible case of a single phase is thus four; that is to say, temperature, pressure and the concentrations of two of the components may be arbitrarily varied within certain limits.

These three-component systems admit of so many possibilities of coexistence of phases that it is out of the question to deal with them here so fully as was possible with two-component systems. It is proposed, therefore, deliberately to omit any consideration of vapour phases, either as regards composition or pressure.

This means loss from the theoretical aspect; but it has justification, not only on grounds of brevity and simplicity, but also from the practical point of view. For in the first place not much work has yet been done on vapour phases in ternary systems, and in the second place, the equilibria between solids and liquids, which have most usually been

studied, are so little affected by pressure that one may generally neglect the error resulting from failure to allow for pressure changes; or, what comes to the same thing, from assuming pressure to be constant throughout a series of investigations and of such a magnitude that a vapour phase does not form. Of course there are cases where such an assumption is not justified; where, for example, an investigation extends over an enormous range of temperatures. But even after setting these cases entirely aside there remains quite a sufficiently extensive field to admit of a student obtaining a very sound introduction to systems of three components. Moreover, there is the very practical point to be considered that in a graphical method of treatment such as that being followed, the number of variables which may be simply represented in a three-dimensional figure is limited. Concentrations of systems may no longer be plotted, as they were in the preceding chapter, along a single axis. Two axes (or a plane surface) are required, so that only one dimension remains for the specification of a third variable, either temperature or pressure. The influence of the latter is so much less than that of the former that a selection of temperature as the more suitable third variable for representation of general cases is inevitable.

Systems in which the pressure is taken to be so high that vapour cannot form are always spoken of as 'condensed systems'. The selection of pressure constitutes the exercise of one degree of freedom, so that in such cases four coexisting phases will constitute an invariant system, three a univariant, and so on. In practical investigations one usually does not trouble to maintain pressure at a particular value. Equilibria between solids and liquids alter so very slightly with moderate or small pressure changes that the effect of failure to maintain the pressure at a chosen value

is generally well within the limit of experimental error in analysis.

Graphical methods. Various methods of plotting the relations between the proportions of three components and the temperature have been, and are, used. In the earlier work of Roozeboom and Schreinemakers, a preference was shown for the method set out in Figure 39.

Temperature is here measured along the vertical axis, while as ordinates and abscissae are taken either the amounts of *A* and *B*, respectively, present for every selected unit of *C* (for example, 100 grammes or a kilogram-molecule) or the proportions (say percentages) of *A* and *B* in a given total of the mixture of *A*, *B* and *C*. Either method serves many purposes, but the former suffers, in particular, from a grave disadvantage in that pure *A* and pure *B* cannot be represented in a finite diagram, since they are given by points infinitely distant from the point of origin o (pure *C*). Both have the disadvantage that the proportion of the third component cannot be read immediately from the figure.

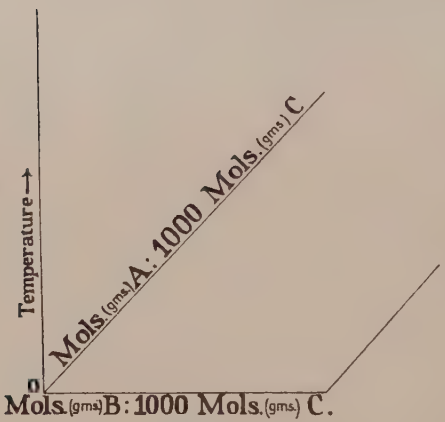


FIGURE 39.

The equilateral triangular diagram. The method suggested originally by Gibbs is free from these defects, and there is no reason at all why it should not be universally

adopted, except just in particular cases where for some special reason other methods give clearer representations. It will be used almost exclusively in the sequel.

Gibbs made use of the geometrical fact that from any point in an equilateral triangle the lines drawn parallel to the respective sides, added together, equal in length each side of the triangle. If then each side be taken as of unit length, the composition of any complex may be represented by a point so chosen that the parallels are the same fractions of the unit length as they are of the total quantity of complex. For convenience, the sides are taken to contain 100 units, and the proportions plotted are then percentages either by weight or by molecule.

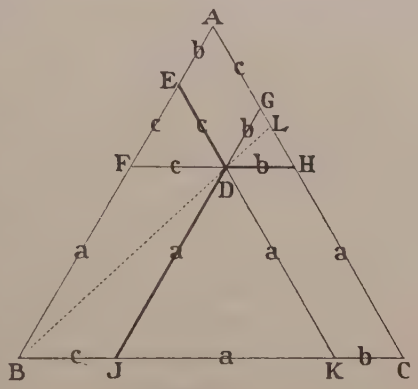


FIGURE 40.

Figure 40 shows precisely how this is applied.

ABC is an equilateral triangle of side equal to 100 units. If those parallels which pass from any point *D* within it to the side opposite the angle *A*, namely, *DJ* or *DK*, be taken as the percentage *a* of component *A*; those to the sides opposite *B* and *C* as the corresponding values, *b* and *c*, of components *B* and *C*, respectively; then it is readily seen from a glance at the various equilateral triangles and parallelograms in the figure that $a+b+c$ equals each of the sides *AB*, *BC* and *CA*, or 100 units. Further, if *D* lie on one of these sides instead of within the diagram,

one of the parallels vanishes and a binary mixture is represented. Thus the point F is that for a mixture containing BF per cent. of A and AF of B. Points on BC represent binary mixtures of B and C, and on AC of A and C. Lastly, if D be coincident with A, B or C, the corners of the triangle, two parallels vanish. It follows that the corners represent the pure single component A, B or C, as the case may be. Temperature may then be plotted at right angles to the plane of the triangle.

All possible mixtures may thus be shown in this triangular diagram, and the proportions of components corresponding with particular points may be read immediately.

The simple principle that if a mixture X is composed of, or can be resolved into, two other mixtures, or components, Y and Z, the points representing the three compositions, X, Y and Z, must lie on a straight line, which is termed a conjugation line, naturally holds in ternary, precisely as in binary, systems. Thus a mixture represented by D in Figure 40 may be regarded as composed of those given by G and J, respectively, in the proportions DJ/GJ of the former to DG/GJ of the latter. Or, again, it may be regarded as composed of pure component B and the mixture L in the proportion $LD/LB : DB/LB$. Moreover, L in turn is seen to have a composition which may be expressed additively in terms of A and C in the ratio $CL/CA : LA/CA$. There will be abundant occasion in the sequel for applying this very simple relation.

In the case of two-component systems, by omission of all complications, Roozeboom developed a comparatively simple model (Figure 12) which illustrated the main possibilities of the case. With three components, even confining attention to concentrations and temperature, this cannot be done so satisfactorily with a single figure, and therefore a succession of models will be employed to show

the most commonly occurring relations. A beginning will be made with systems in which solid and liquid phases are present in equilibria of the simplest types.

Simplest equilibria between solids and liquids. In Figure 41, which aims at showing a three-dimensional concentration-temperature diagram in perspective, A_1 is the melting-point of pure component A, B_1 of B and C_1 of C. The triangular prism is cut into two portions by the three surfaces A_1pEr, B_1qEp and C_1rEq, which meet in pairs along pE, qE and rE.

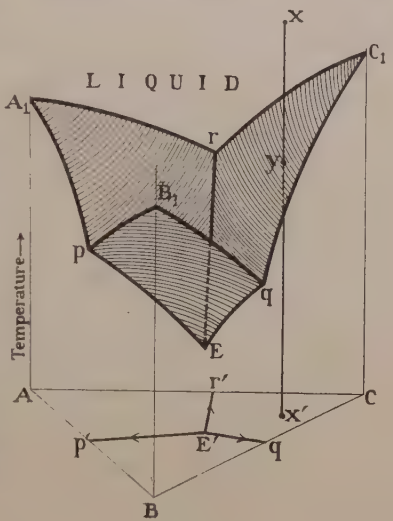


FIGURE 41.

Any system represented by a point in the upper part is entirely liquid. This is a single-phase region. Below the surfaces a number of polyphase regions exist, each with perfectly definite limits and all fitting together to make up the lower part of the prism.

The dissection of the model offers little difficulty. Starting from A_1 where liquid and solid pure A coexist, addition of B will in general give a solution of it in A which will be in equilibrium with solid A at a temperature lower than A_1 in proportion to the amount added. At p no more B will dissolve in the melt, but solid A, B and solution will coexist. This, therefore, is the binary eutectic of Figure 25 (Chapter IV), A_1p being joined here by the similar curve

B_1p. A_1pB_1 lies, of course, entirely in the vertical plane above AB, where the ternary system merges into one of its three constituent binary systems.

If now to the eutectic p in equilibrium with solid A and solid B there be added some of the third component C, the same phenomena may be expected as are found in the two-component case. The added C will dissolve and this solution will remain in equilibrium with solid A and B, but at a lower temperature than that of p. Therefore the curve showing the composition of the melt progressively alters in a direction downwards. A point E will ultimately be reached at which no more C will dissolve. Here, then, three solids and a liquid are in equilibrium. It may be termed a ternary eutectic point and, there being four phases present, it is a (condensed) invariant system. Strictly speaking, four phases constitute a univariant system, but one degree of freedom has been exercised in this case in a selection of pressure. If, therefore, other pressures be exerted upon this system of phases, they may coexist at certain other temperatures than that of E in Figure 41. The effect of pressure, however, is very small indeed.

Just the same argument may now be applied in explanation of the sets of curves B_1q, C_1q and qE on the one hand, and A_1r, C_1r and rE on the other. One must bear in mind that these curves are merely the boundaries of the three surfaces which together make up the lower limits of that portion of the prism, the (condensed) tervariant system, in which the single unsaturated liquid phase exists. Once a liquid mixture of composition x' has fallen from a temperature at the level x to one at the level y lying on one of these surfaces the liquid has reached the saturation limit and further cooling results in the separation of one or more components as solids. A_1pEr, B_1pEq and C_1rEq may therefore

be termed 'saturation surfaces', the solid phases with which liquids lying on them are saturated being A, B and C, respectively. Should the liquid composition fall on a line pE, qE or rE, common to two surfaces, it is simultaneously saturated with respect to two of these components, either A and B, B and C or A and C as the case may be. When of the composition E, it is saturated with respect to all three.

Continued cooling to points below these three saturation surfaces will result, then, in phase reactions taking place with production of complexes of liquid in equilibrium with one, two or three solids, yielding systems ranging therefore, under a fixed pressure, from bivariance to invariance.

There are three regions such that any mixture represented by a point within them separates into a bivariant system of solid and liquid. The first, in which the solid is A and the liquid may lie anywhere on the surface A_1pEr, is bounded by that surface and such others as will be traced out by a straight rod of adjustable length moving horizontally with one end on the vertical line AA_1 and the other passing continuously from A_1 to r, thence to E, to p and back again to A_1. The second, in which the solid is B, is bounded by the surface B_1pEq and the trace of a similar horizontal rod or line connecting some part of BB_1 with successive points from B_1 to q, thence through E to p and back to B_1. In the third, the solid is C and the bounding surfaces may be described similarly.

There are also three univariant regions or spaces, any complex within which separates into liquid and two solids. The first, where the solids are A and B and the liquid is somewhere along pE, is best described as that marked off by a series of horizontal triangles with apices passing successively from p to E, and bases of length AB. The

second and third may be described similarly with respect to qE and BC in the one case, and rE and AC in the other.

Lastly, there is an invariant system consisting of the horizontal plane passing through E. At the temperature of this plane any ternary complex will give liquid E and the three solids, A, B and C.

As to the region below the level of E, so far as ordinary experiment will show, A, B and C may coexist in any proportions. As there are three phases, the region is, strictly speaking, univariant when pressure is fixed. This means that compositions may vary with temperature, but for the present, as already admitted, strict analysis of the question of compositions of solid phases is being avoided. It is a useful exercise for a student to make perspective drawings of all these sections of the prism.

Summarizing, we have the following (condensed) systems:

One tervariant: liquid.

Three bivariant: one liquid and one solid.

Four univariant: three of them with one liquid and two solids, the fourth with three solids.

One invariant: one liquid and three solids.

Altogether, the ternary prism has been divided into eight distinct portions belonging, respectively, to the eight systems first mentioned. The ninth (invariant) system is a plane.

Isothermal sections of Figure 41. A series of (isobaric) isothermal sections of general type may immediately be deduced from Figure 41. At temperatures above C_1 all possible proportions of A, B and C fuse to homogeneous liquids. Figure 42 shows the system at a temperature below C_1 but above A_1.

All complexes of composition falling within the area *ABba* are liquid ; those falling in *abC* separate into two phases, of which one is solid *C* and the other a liquid along the curve *ab*. Thus, the complex *c* gives solid *C* and solution of composition *d*, the proportion of solid being *cd/dC* of the total, and of liquid *cC/dC*.

The area *abC* is obviously a portion of one of the bivariant spaces described above. In the isothermal section, however, one degree of freedom has been exercised in the selection of temperature, so that *abC* is a univariant system, or to be quite definite, an isothermal, condensed univariant system. One must continually bear in mind the fact that the variance or residual variance of a specified system depends not only upon the number of phases present, but also upon the number of degrees of freedom which have already been exercised in defining the particular conditions under which the system is being examined.

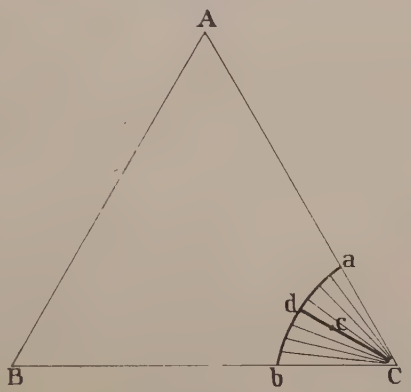


FIGURE 42.

The shape of any saturation curve such as *ab*, and hence of the surface of which it is a part, cannot be predicted. It depends, *inter alia*, upon the structure of the liquid, that is to say, upon the presence of, and the proportions between, simple or compound molecules, or ions, or whatever may be formed there from the components. Into such matters the theory of phase equilibria does not enter. It is con-

cerned only with the limits of such curves and not at all with their shapes.

Between the temperatures A_1 and r there is a similar appearance of a heterogeneous area extending from A, and at r the two meet as shown in Figure 43.

This is the only temperature at which the two solids A and C can coexist with a liquid which is the mixed melt of these two components only. At lower temperatures they can exist only with liquids containing B as well. Hence subsequent isotherms are of the type of Figure 44, taken a little below the temperature B_1, where therefore there is the further change of a new region *Bde* of complexes yielding solid B and solution.

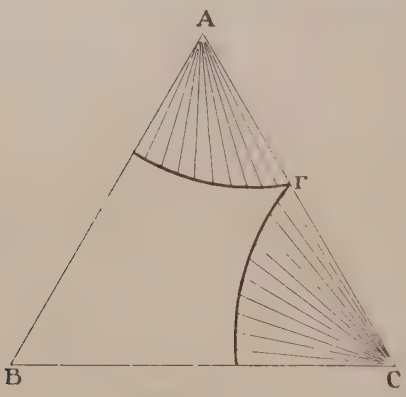


FIGURE 43.

There are now three areas all compositions in which give heterogeneous or two-phase systems, namely, *Cab*, *Aac* and *Bde*. Complexes falling in the area *Aac*, which is a portion of one of the univariant spaces previously described, resolve themselves into three phases, namely, solids A and C and the liquid a. Three phases possess two degrees of freedom. In Figure 44 both have been exercised in settling pressure and temperature. The system is therefore (isothermal, condensed) invariant. So long as temperature and pressure are maintained constant, the compositions A, C and a are invariable. Complexes falling in the area *abedc* remain completely liquid.

At still lower temperatures, c and d approach and meet at p (Figure 41): e and b at q (ibid.). Below these respective temperatures the changes are similar to those which occurred below r in Figures 41 and 43. Hence, an isothermal section below both p and q, but above E, has the form of Figure 45.

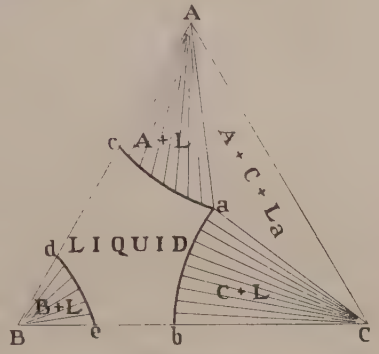


FIGURE 44.

No binary mixture can any longer be liquid. The liquid ternary mixtures are those of compositions falling in the area *abc*. The two-phase (liquid and solid) areas are *Aac*, *Bbc* and *Cba* respectively. The three-phase (two solids and one liquid) areas are *Aac*, *Bbc* and *Cab*.

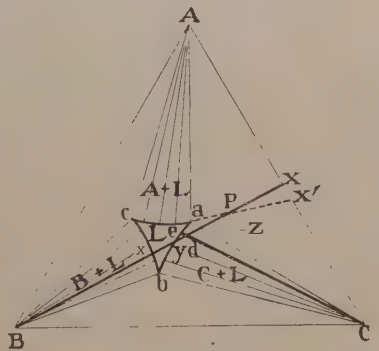


FIGURE 45.

The sections at temperatures lower still show a continuation of the decreases in the single and double phase areas. At E these have shrunk to a point and lines respectively, and below E they have vanished: solids alone may exist.

Changes with alteration of composition. The changes which occur as the composition of a complex is steadily varied may be read immediately from any of these iso-

therms. An example will be taken from Figure 45. X is a mixture of solid A and of solid C, containing CX per cent. of A and AX per cent. of C. Successive additions of B to it give complexes represented by points along the line XB. On the first addition of B, the stable phases are liquid a and the solids A and C, portions of which must therefore melt to form with B this liquid. The proportion of liquid steadily increases as the amount of B increases. When the mean composition of the system is that of the point P, the fraction PX'/aX' will be liquid of composition a, and the remainder, aP/aX', will be what remains of the original solid mixture of A and C, now containing only CX' per cent. of A, but AX' per cent. of C. Thus, in this particular case, more A than C has dissolved on addition of B. The relative amount of A in the solid continues to diminish until at z it becomes zero. The system then gains a degree of freedom, changing from (isothermal, condensed) invariance to univariance. The composition of the liquid may be varied while the equilibrium remains one of two phases, liquid and C. Thus, between z and y the system contains a liquid of concentration steadily changing from a to y, and a solid which is pure C. The amount of solid decreases as B is added, the proportions between solid and solution at any stage being immediately ascertainable. Thus, at d, ed/eC of the total is there as solid C; dC/eC as liquid of composition e. At y the solid phase vanishes, and any more B added dissolves completely, there being but a single liquid phase up to the point x. This point x, an (isothermal, condensed) univariant system, represents the limit of solubility of B, and any more added merely remains as solid. The changes have therefore been from a two-phase (solid-solid) system at X to a three-phase (solid-solid-liquid) along Xz; thence to a two-phase (solid-

liquid) along zy and to a single-phase liquid along yz, ending at last in a different solid-liquid system along xB.

Compound formation between components. It is seldom that a ternary system exhibits the simplicity of Figure 41. Cases of it are found with metals, a good example being that in which the components are lead, bismuth and tin. But, as a rule, one finds the added complications that come from the formation either of compounds or of mixed crystals between some or all of the components. So many highly important systems are of the kind where compound formation occurs, that typical cases of some consequential modifications of Figure 41 and of selected isotherms will now be considered in detail.

As the simplest example, one may take a case where two of the components, say A and B, are able to form a single compound, A_mB_n. Figure 46 shows one of the resulting modifications of the three-dimensional model. In this it has been assumed that the compound A_mB_n is stable throughout the whole temperature range.

A_1, B_1 and C_1 are, as before, the respective melting-points of the pure components; H_1 that of the compound A_mB_n. The form of the curve on the limiting plane above AB is that of a two-component system already exemplified in Figure 26 (Chapter IV) showing two eutectics.

At r_1 the solid phases are A_mB_n and A; at r_2, A_mB_n and B. Addition of C lowers the temperatures of both equilibria; the former to E_1, where it meets the curve qE_1 of the lowering of eutectic $A-C$ by addition of B; the latter to E_2, where it meets pE_2. E_1 and E_2 are therefore both ternary eutectics, the systems of solid phases being $A-C-A_mB_n$ and $B-C-A_mB_n$, respectively.

These systems of three solids and a liquid do not possess any degrees of freedom when pressure has been fixed. When, therefore, temperature is altered, one phase must go. The equilibrium will be that of an equation showing three solids on one side and the liquid on the other. Liquid is produced when heat is added so that one solid disappears. Hence, three curves (each giving compositions of liquids coexisting with two solids) must proceed upwards from each of the points E_1 and E_2. One of these in each case will be for the system $C - A_m B_n$ — liquid, and the two must form a continuous curve. In other words, the curve connecting E_1 and E_2 in Figure 46 must pass through a maximum as shown. It cannot run directly from one eutectic to the other.

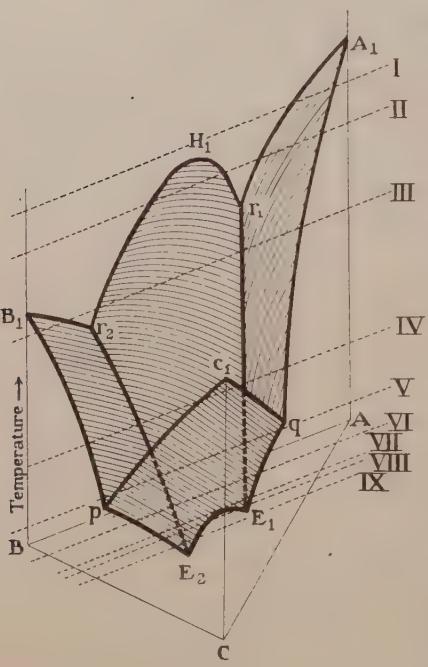


FIGURE 46.

Isothermal sections of Figure 46. Even though this solid figure is very like Figure 41, it is worth while to show the precise types of sections of it taken at different levels of

temperature. At that marked I the type* is that of Figure 42, but at all lower levels the compound A_mB_n gives rise to differences. Figure 47 is the isotherm at the level II. All mixtures are liquid except those which fall in the areas *Aab* and *cde*. The former separate into solid *A* and a solution somewhere on *ab*: the latter into solid A_mB_n and a solution on *ced*. Lowering of temperature increases the areas of heterogeneity and a section at r_1 (Figure 46) would show *a* and *c* coinciding. Below this, as at the level III, the isotherm is of the type of Figure 48.

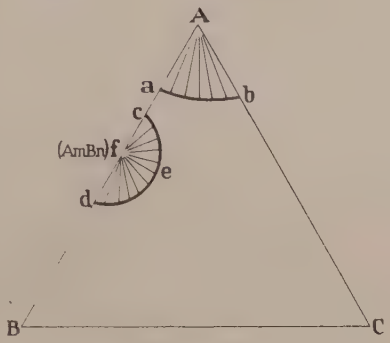


FIGURE 47.

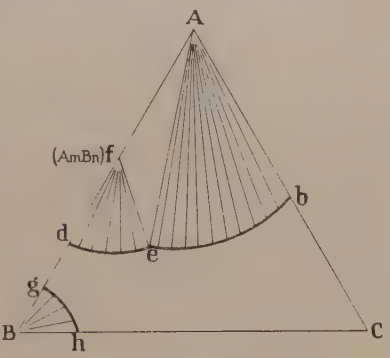


FIGURE 48.

A solution of composition *e*, which is on the curve r_1E_1 of Figure 46, is in equilibrium with both solid *A* and A_mB_n. Any mixture of *A*, *B* and *C*, having a composition falling in the triangle *Aef*, will at equilibrium consist of solution *e* and a mixture of solids

* In these sections no attempt is made to retain the relative proportions of the various regions of Figure 46: illustration of types only is aimed at.

A and A_mB_n. No mixture of these solids will melt to give a liquid phase alone. *de* is the curve of solutions that can exist with A_mB_n, *eb* of those with A, and *gh* of those with solid B. At r_2, g and d coincide. At C_1, and below it, solid C appears. At the level marked IV, the section is as shown in Figure 49. Any complex falling in the new triangle *Bkf* gives solution of composition k and a mixture of solids B and A_mB_n. The area of heterogeneous phases A and solution, *Aeb*, is becoming smaller.

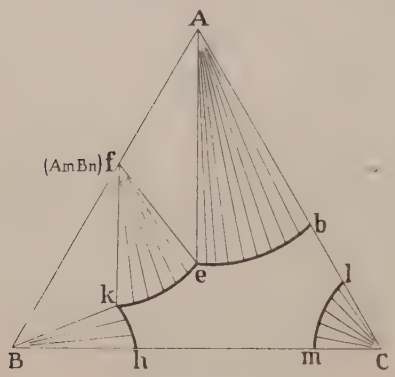


FIGURE 49.

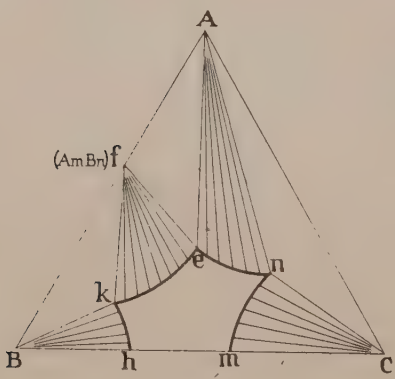


FIGURE 50.

At q, l and b coincide. Below q, as at the level V, the isotherm type is given by Figure 50.

Liquid binary mixtures of A and C are no longer stable. Any complex lying within the triangle *AnC* consists of liquid of composition n and a mixture of solids A and C. The region of existence of unsaturated liquid mixtures has been reduced to that enclosed by *hkenm*. This shrinks still further as the

temperature falls. *h* and *m* steadily approach one another and so do *e* and *n*. At the temperature of *p*, *h* and *m* coincide, and liquid binary mixtures of *B* and *C* cannot exist below it.

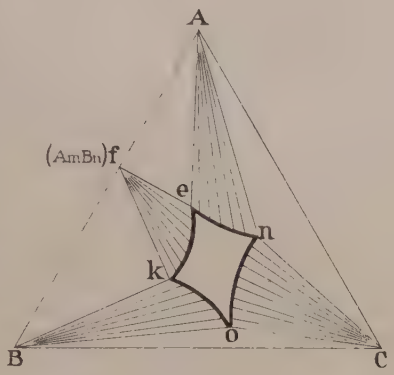


FIGURE 51.

Below *p*, but above E_1, the section (VI) cuts across four saturation surfaces and there are four (isothermal, condensed) invariant points, *k*, *e*, *n* and *o*, as seen in Figure 51.

The region *keno* of unsaturated liquid phase is shrinking, but with further fall of temperature it does not decrease steadily to zero. Instead, the two curves *ke* and *no* approach one another and at the level of VII (Figure 46), which is the maximum point of the curve E_1E_2, they touch as shown in Figure 52, giving a single solution, *S*, saturated with both *C* and A_mB_n and dividing the area of unsaturated liquid into two parts, *ens* and *kos*.

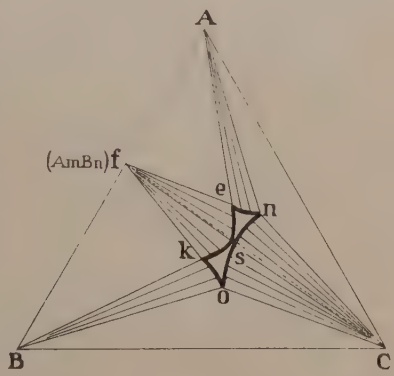


FIGURE 52.

Then below this maximum point, but still above both E_1 and E_2, at, say, the level VIII, this separation becomes complete, the isotherm taking the form of Figure 53, which may be divided into two similar portions by the line *Cf*.

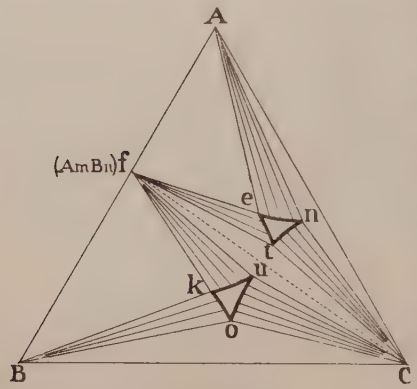


FIGURE 53.

Comparing this with Figure 51, which is section VI of Figure 46, it will be seen that the curve *ke* in the latter is now represented by only the two end portions *ku* and *et*: similarly *on* by *ou* and *nt*. What were three areas have thus now been divided into six by the interposition of a seventh area *fuCt*, complexes falling within which resolve themselves into solid A_mB_n and solid *C* with one or other of the solutions *u* or *t*.

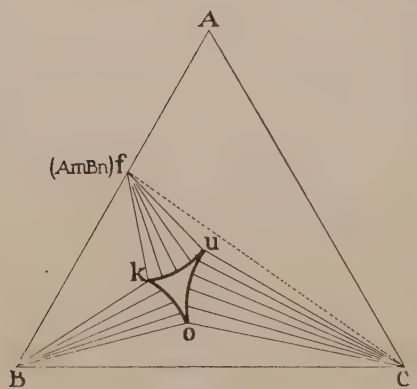


FIGURE 54.

At E_1 (Figure 46) *e*, *t* and *n* of Figure 53 meet in a point, the two-phase areas *Aen*, *fet* and *Cnt* diminishing to lines. Thereafter the solid phase *A* cannot exist in

equilibrium with any liquid, and the isotherm is that shown in Figure 54 (level IX in Figure 46).

At E_2 the limit of existence of any liquid phase is similarly reached, the isotherm containing just a single point. All ternary complexes at this temperature will give a solution of the composition of this point together with the three solids B, C and A_mB_n.

The precise description of the boundaries of all the polyphase systems in the prism of Figure 46 should now not present any difficulty.

Modifications of Figure 46. Besides this case, where the compound A_mB_n is stable throughout the whole temperature range, there are two other possibilities to which it is worth while to draw attention, without staying to go into detail. The one is exemplified in Figure 55 and shows a lower temperature limit, T', to the existence of the compound. The other, Figure 56, shows a case where the compound only comes into existence in the lower part of the temperature range, at a point also marked T.

In both cases we have at T a (condensed) invariant system of four phases, three solids, A, B and A_mB_n, and a liquid, and it is easy to see that the reactions at these points may be represented by the equation

$$A + B \rightleftarrows A_mB_n + \text{liquid}.$$

In Figure 55 rise of temperature causes the action to proceed from left to right with disappearance of A or B: in Figure 56 from right to left, with disappearance of A_mB_n. The liquid phase does not disappear in either case whatever the direction of the temperature change, so that T' is a transition point between solids and not a eutectic point.

Common projections. While it is very advisable for a student to study with the aid of space models or perspective

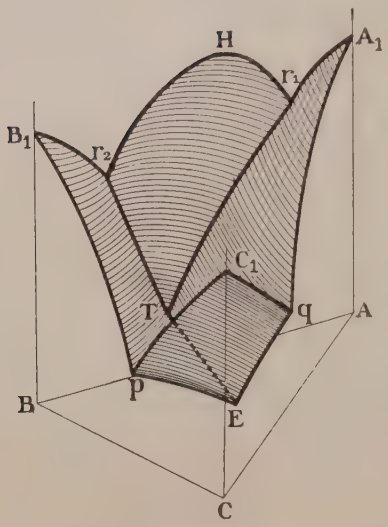


FIGURE 55.

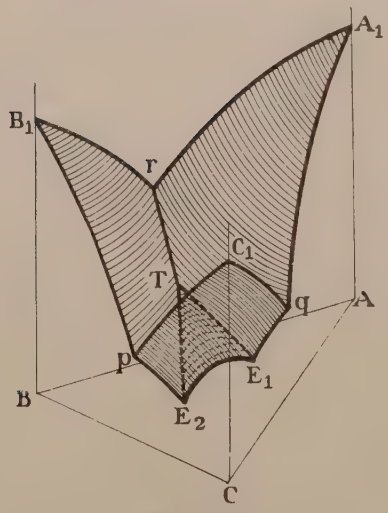


FIGURE 56.

drawings the principles underlying these ternary systems, there are occasions when it may be more convenient to use projections. The two in most common use are the orthogonal projection downwards on the triangular base, and the perspective horizontal projection on to one side of the prism from the opposite vertical edge. The first method is used very often by Schreinemakers, and an example is seen on the base triangle of Figure 41. The significance of the three curves and the four eutectic points (three binary and one ternary) is obvious. No information regarding temperature is given, though the direction in which temperature increases as concentrations alter may be, and usually is, shown by arrows.

The second method is

illustrated in Figure 57, which gives the projection of Figure 46 on the vertical plane B_1BAA_1 from successive points along the line CC_1 and upwards.

It is advisable for the student to work out for himself the limited significance of the divisions in the projection as compared with those of the full Figure 46. Jänecke first suggested this type of projection. It can give only a portion of the information contained in the space model, but is very useful for tracing the courses of certain changes in phases with alteration in temperature. From the present point of view it is not necessary to consider it further.

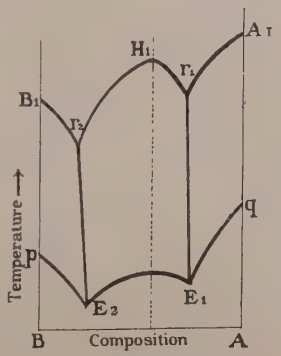


FIGURE 57.

The discussion of these relatively simple cases may be taken to indicate the lines upon which still more complicated systems than those of Figure 46, &c., may be worked out. The general treatment is similar when A and B can form more compounds than one and when B and C, or C and A, or both, form one or more compounds, or when ternary compounds may exist.

The literature of the subject abounds in illustrations incompletely worked out. It is seldom that more than a few isotherms are determined: two or three usually suffice to give a reasonable lead as to the form of a required part of the complete three-dimensional figure. In particular, a great deal of attention has been devoted to cases where one component is a salt and the other two are solvents, or two are salts and the third a solvent; and such investigations are usually limited to temperature ranges

above the freezing-points of the solvents. It is perhaps worth while to consider a few isolated isotherms of this kind and to take the opportunity to discuss certain practical points in the use of triangular diagrams.

Some typical isotherms: solvate formation. Figure 58 is an example of a system in which the salt S is able to form with one solvent W (say water) several compounds (hydrates) of compositions represented at H_1, H_2 and H_3, but is unable to form a compound with the other solvent A (say alcohol).

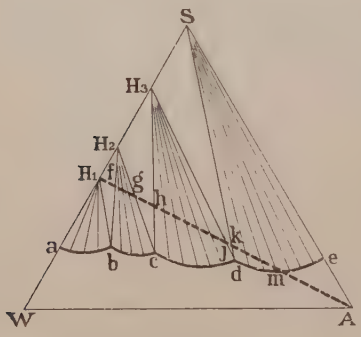


FIGURE 58.

There are four distinct solubility curves. Solutions along the first, *ab*, are saturated with respect to hydrate H_1; those along *bc* with respect to H_2; *cd* to H_3 and *de* to S. *b*, *c* and *d* are solutions in equilibrium with the pairs of solids H_1 and H_2, H_2 and H_3, and H_3 and S, respectively. From the diagram one can tell at once how any mixture of the three components will resolve itself at equilibrium, and in illustration one may take the changes which will occur when solvent A (alcohol) is added in successive amounts to the hydrate H_1. The average compositions of the mixtures so formed will lie along the line H_1A.

On first addition of A, dissociation of some H_1 occurs, giving rise to solution of composition *b* and formation of some of the lower (that is, less hydrated) compound H_2. This three-phase system will persist, with steady increase in amount of H_2 and decrease of H_1, until the point *f* is

reached where the line $H_1 l$ cuts $H_2 b$. Here the amount of H_1 has dwindled to zero and the system is one of two phases, solution b and H_2. This solid phase persists as more alcohol is added, but the solution steadily passes from composition b to c. Beyond the intersection g, the third hydrate, H_3, makes an appearance, and between g and h the three phases H_2, H_3 and solution c are in equilibrium, the amount of H_3 steadily increasing as H_2 diminishes. At h, H_2 has vanished, and between h and j, H_3 exists with solutions continuously changing from c to d. Between j and k, the third three-phase system occurs, the solution being d and the solid H_3 and the anhydrous salt. At k the former vanishes, and from k to m the latter is in equilibrium with successive solutions from d to m. At m the salt has entirely dissolved and further addition of alcohol gives unsaturated solutions only.

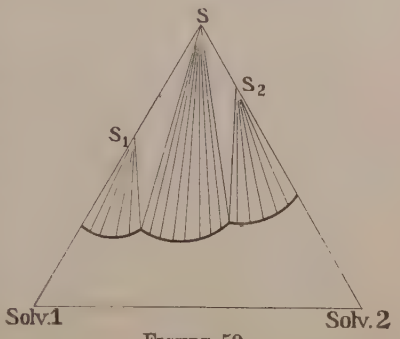


FIGURE 59.

In following this sequence of changes one has dealt of course only with systems that are in stable equilibrium. If the attempt were made to realize this sequence experimentally, metastable conditions would certainly be passed through before the final states were established.

When both solvents are able to combine with the salt chosen as third component, the form of the isotherm is that shown in Figure 59, if only one solvate exists in each case. This offers nothing new (from the point of view of interpretation) as compared with Figure 58.

In both these cases the two solvents have been supposed miscible with one another in all proportions, and at the temperature selected there has not been any separation of a liquid phase into two immiscible liquids of different compositions. Instances occur where neither condition is fulfilled.

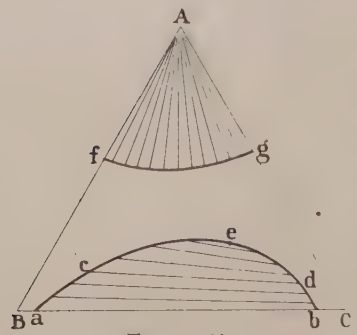


FIGURE 60.

Partially miscible liquid components. Figures 60 and 61 illustrate a case where component *A* is soluble in each of the solvents *B* and *C*, which are only partially miscible with one another.

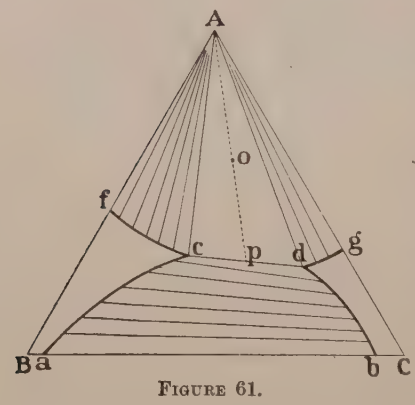


FIGURE 61.

In Figure 60 *a* and *b* are concentrations of the two layers formed by mixing *B* and *C* in any proportions given by points along *ab*. Addition of *A* may or may not cause the layers to approach one another in composition. It has been assumed in the figures that the miscibility does increase as *A* is added, giving steadily approaching layers, as at *c* and *d*, which become identical at *e*. *fg*, lying above the curve *acedb*, gives solutions in equilibrium with solid *A*.

Figure 61 represents the same system at a different temperature where the curves intersect. There is no longer

a continuous series of solutions in equilibrium with solid *A*, but at *c* a second liquid layer of composition *d* appears, the two being able to exist in equilibrium. All mixtures of average compositions represented by points within the triangle *Acd* will resolve themselves into solid *A* and these two liquid layers. Thus, of a complex *o*, the fraction *op/pA* will be solid *A*, and *oA/pA* will be in the liquid layers, of which the proportion *dp/dc* will be in the layer of composition *c*, and *cp/cd* in that of composition *d*. Complexes beyond *Ac* and *Ad* will give solid *A* and single solutions. Those within *acdb* will of course give two liquid phases and no solids, and a fuller treatment of such cases will be given presently.

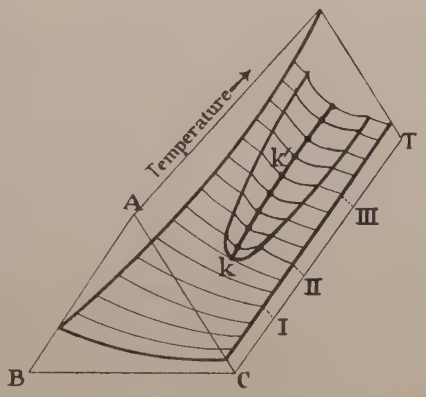


FIGURE 62.

Partially miscible ternary liquids. A somewhat similar case to this may occur even when the two solvents are miscible in all proportions. At certain temperatures and in the presence of certain proportions of the third component *A*, two liquid phases may appear. Figure 62 shows in perspective the concentration-temperature space model of such a system.

In the lower portions, as at *I*, the isothermal section is similar to the upper part of Figure 60. At *k* the first sign of a separation of the solution into two layers appears.

At higher temperatures, as at *III*, the section is that of Figure 63. The regions *Afc*, *Acd* and *Adg* do not differ from those similarly lettered in Figure 61; but with increase in the amounts of *B* and *C* the two liquid layers approach in concentration and ultimately coincide at *k*.

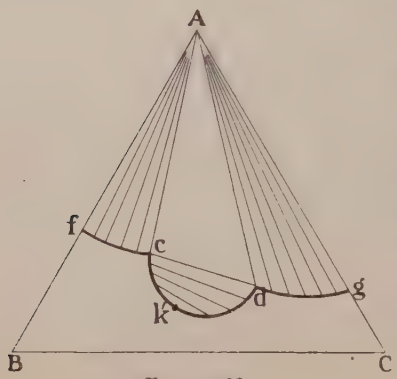


FIGURE 63.

Other common types of isotherm. A system of one solvent *B* and two soluble components *A* and *C*, each of which may form a solvate (S_A and S_C), and which may unite to form a molecular compound (S_{AC}), such as a double salt, is illustrated in the isotherm, Figure 64.

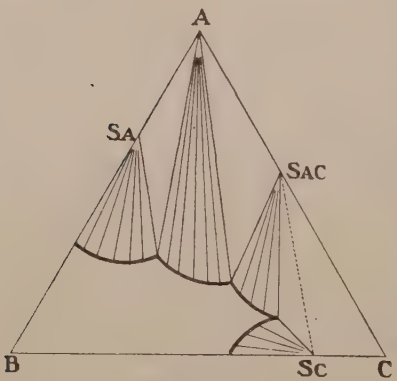


FIGURE 64.

Where a ternary compound may be formed the diagram includes a portion such as *abc* in Figure 65, where *c* gives the composition of this compound. Complexes in the triangle *AcC* resolve themselves into solids only, namely, *A*, *C* and the ternary compound, in proportions at once calculable.

Finally, in Figure 66 is an actual case in which the components are water, sodium oxide and chromic anhydride at a temperature (20° C.) where no less than eight different solid phases may exist according to the proportions between

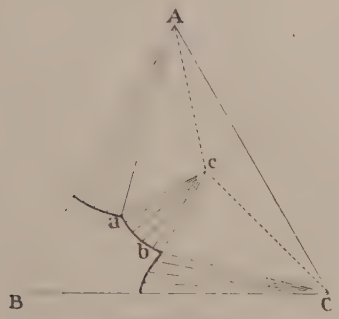
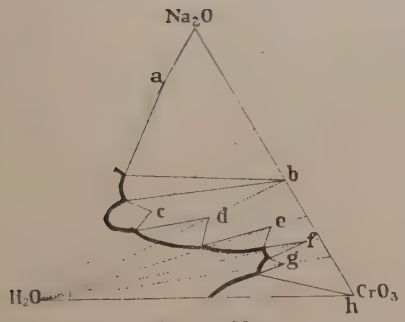


FIGURE 65.



(*a*) $NaOH \cdot H_2O$.
(*b*) $Na_2O \cdot CrO_3$.
(*c*) $\frac{1}{2}Na_2O \cdot CrO_3 \cdot 13H_2O$.
(*d*) $Na_2O \cdot 4CrO_3 \cdot 4H_2O$.
(*e*) $Na_2O \cdot 2CrO_3 \cdot 2H_2O$.
(*f*) $Na_2O \cdot 3CrO_3 \cdot H_2O$.
(*g*) $Na_2O \cdot 4CrO_3 \cdot 4H_2O$.
(*h*) CrO_3.

FIGURE 66.

these components (Schreinemakers, *Zeit. phys. Chem.*, 1906, **55**, 71). This diagram will afford good exercise in interpretation in the light of the general discussion which has been given.

Determination of compositions of solid phases. To arrive at a knowledge of the exact solid phase, or phases, in

equilibrium with a particular solution is an essential part in the determination of such systems as these. After separating the solid by filtration, or other means, it is often a troublesome matter to free it completely from adhering solution, keeping the whole exactly at the temperature of the isotherm sought.

A simple graphical procedure, dependent upon the use of conjugation lines, enables one to avoid the necessity for this. The method may be illustrated from Figure 67.

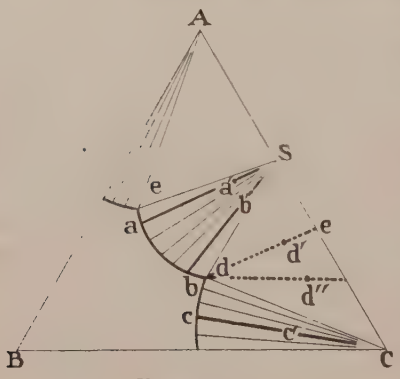


FIGURE 67.

a is a solution in equilibrium with a solid of unknown composition. By filtration, a portion of moist solid, that is, solid and adhering solution, is removed. Devices for maintaining constant temperature during filtration will be necessary or not according to the temperature of the isotherm and the rate at which filtering can be carried out. A known weight of moist solid, or residue (German *Rest*), is then analysed. Since it is a mixture of the solution *a* and the pure solid, its composition, represented at *a′* in the figure, must lie somewhere on the straight line connecting those of solution *a* and of pure solid. The more completely adhering solution has been removed in the filtration, the nearer will it lie to the latter. The composition of the solid is therefore somewhere on *aa′* produced. By an exactly similar argument, this composition will be on *bb′* produced. The intersection of the two lines, the point

S, therefore gives at once the desired value, and other solutions and residues will confirm, or correct, the point. Thus one arrives at a knowledge of the solid phase without requiring to obtain it perfectly pure for analysis. The procedure may be termed the Residue (or *Rest*) Method.

If the chemicals dealt with are quite pure, there is no occasion even for an analysis of a residue. A complex, or mixture of components, in exactly known proportions is prepared and allowed to pass to the equilibrium condition. Then, referring again to Figure 67, if c' be the mean composition of the complex and c that of the solution formed, the composition of the solid phase must lie on cc' produced. From a similar set of figures for another complex and solution, an intersection giving the composition of the solid is obtained just as before.

This method is rather simpler than the preceding one, but in practice it is seldom preferred because usually it is advisable to take the complex fairly near to the solution point, so that the extra-polation becomes a lengthy one, and errors in composition of either solution or complex are magnified in that of the solid. Nevertheless it might be employed with success much more than is done.

Intersection of solution curves. It is to be pointed out, in passing, that all complexes, or residues, lying in an area like the triangle *SdC* of Figure 67, will resolve themselves into a solution and a mixture of solids. Thus d' gives the fraction ed'/ed of the total as solution d, while $dd'de$ consists of solids of which Ce/CS is the double salt S and Se/SC is the component C. When two complexes, as at d' and d'', give the same solution, as at d, it is evident that d is a point of intersection of two solution curves.

Practical points in preparing pure solid phases. When, however, it is desired for some reason to obtain a pure

solid, say a pure double salt such as D_1 or D_2 in Figure 68, free from admixture with the solution with which it is in equilibrium, one can often obtain from an isotherm useful guidance as to procedure.

Suppose B is a solvent, such as water, A and C being salts capable of forming the double compounds D_1 and D_2.

Filtration of a complex containing solution and either of the double salts will give the solid with more or less adhering solution. The natural next step might be to wash the crystals rapidly with water, then removing residual water as quickly as possible by suitable means. Provided that these operations can be carried out so fast that no progress towards a new equilibrium is made, the result will be satisfactory. Otherwise the result will vary according to the relative positions of the curve giving solutions in equilibrium with the double salt, the point corresponding with the composition of the double salt, and the angle representing pure water. Thus in Figure 68 if impure D_1, of mean composition given by a point just inside the triangle D_1ae, be treated with water so as to give a complex of mean composition falling as at c within the triangle D_1eD_2, a change will occur, and will become more or less complete according to the time available, giving solution e and a mixture of the solids, D_1 and D_2. In other words, the double salt D_1 is decomposed by water and

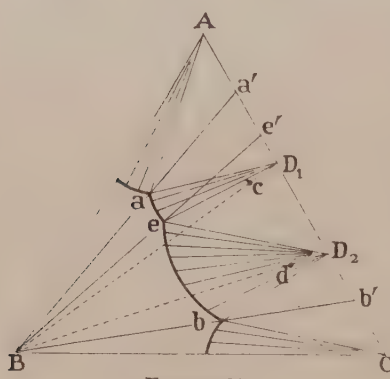


FIGURE 68.

the latter should therefore be avoided for purposes of washing. On the other hand, the line joining D_2 or a point near it cuts the curve *eb*, and therefore a complex, such as *d*, cannot give rise to any other solid. Washing with water will therefore be less objectionable in this case.

Finally, there may be cases where it is advisable to allow complete equilibrium to be attained in the complex formed by addition of water to one substance *A* which is contaminated by another, *C*. Such contamination may have been brought about by overcooling a solution depositing *A* to a point at which both *A* and *C* may deposit together. In Figure 69, which is an isotherm for water (*B*), *A* and *C* at about ordinary temperature, the point *M* represents (to an exaggerated extent for the purposes of the diagram) such a product.

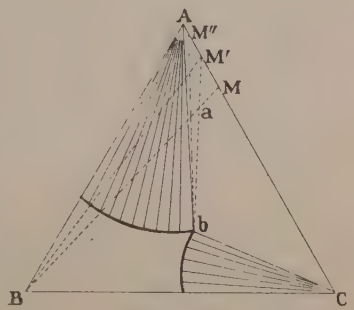


FIGURE 69.

Addition of water to *M* gives a complex represented at *a*, say, and this resolves itself into solution *b* and solid *M′*. The latter is very much nearer to pure *A* than *M*, and repetition of the same procedure will give a product *M″* still closer. Moreover, a knowledge of the proportions in which *M* and water are mixed will enable one to calculate at once from the diagram the 'yield' of *M′* and the quantity of solution *b* formed. Such a process of 'steeping' or 'soaking', if practicable, is very much to be preferred to what is ordinarily termed 'purification by recrystallization' and which involves first the complete solution of the whole

impure mixture at a suitable temperature, and then separation of the pure solid by cooling. Especially in large-scale work is the avoidance of these operations desirable.

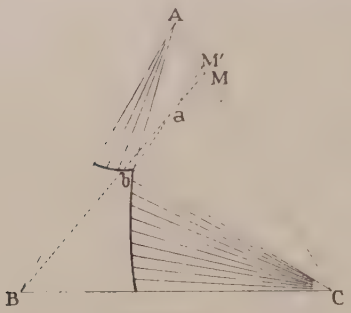


FIGURE 70.

It may, however, happen that 'steeping' will lead to little or no purification, or even to a relative increase in impurity; and again the required information may be obtained from a suitable isotherm. Thus in Figure 70, if *M* be steeped with water in proportions giving the complex *a*, there will be formed solution *b* and a solid *M′* hardly differing at all from *M*: while in Figure 71, steeping the impure product *M* may lead to *M′*, containing actually an increased percentage of the impurity *C*. In such a case purification by steeping is no longer practicable.

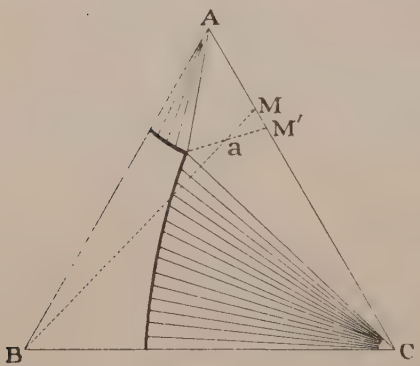


FIGURE 71.

'Congruently' and 'incongruently' saturated solutions. It is pertinent at this point to return to Figure 68 in order to draw attention to the presence of two very different types of (isothermal, condensed) invariant systems.

There are three invariant points in the figure, namely, a, e and b. If a conjugation line be drawn from B through each of these points to the side AC, it is at once clear that a and b are similar systems, while e belongs to a different type. The differences appear in two respects. In the first place, the composition of solution a (or, *mutatis mutandis*, of b) may be expressed in terms of the solvent B and a mixture a' of the solids, A and D_1, with which the solution is in equilibrium. In the next place, evaporation of B from a will give a complex of mean composition lying on the line aa', which means that A and D_1 will both separate out during the process. Such a solution is commonly said to be 'congruently' saturated with respect to the two solids.

By contrast, the composition of e cannot be expressed in terms of the two solids, D_1 and D_2, with which it is in equilibrium, and the solvent B. No line connecting B and any point on D_1D_2 passes through e. Again, evaporation of B from e gives a complex lying in the area aeD_1, not in D_1eD_2. The solid separating will then be D_1 alone, not a mixture of both the solids with which e was saturated. The reaction occurring during evaporation results in the disappearance of D_2 as a solid phase (if any be present initially with e), with production of solution lying along ea. Such a solution as e is said to be 'incongruently' saturated with respect to the two solids. These terms are in very general use.

General case of partial miscibility of one pair of liquid components. In the examples so far treated, the general type of equilibrium has been that between one or more solids and a solution. It was convenient to illustrate in Figures 60, 61, 62 and 63 the modifications introduced into particular isotherms when two liquid phases appear, but

the general case of partially miscible liquids requires rather fuller treatment. It will suffice to consider a selection of the possible cases, taking first those where one, then those where two, and, lastly, those where all three pairs of liquid components are at certain temperatures only partially miscible. Figure 72 is an example of the first kind.

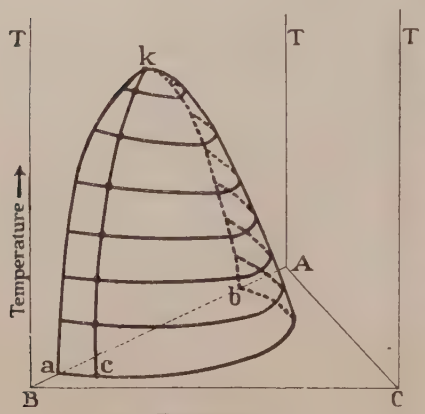


FIGURE 72.

A and *B* are partially miscible; *B* and *C*, and *A* and *C*, wholly. All isothermal sections below *k* are of the type of Figure 73.

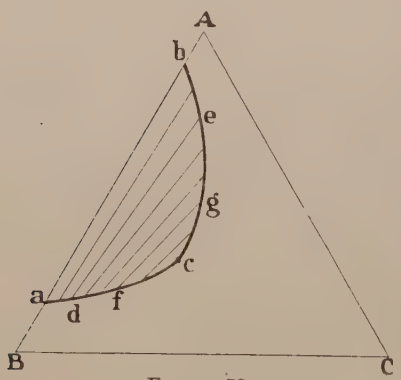


FIGURE 73.

Here *a* and *b* are the two liquid layers formed by any binary mixture of *A* and *B* in proportions represented by points lying on the line *ab*. Mixtures falling on *Ba* or *bA* are homogeneous or single-phase. Such cases of binary systems in two liquid layers were not discussed in Chapter IV, to which they properly belong: the present brief account of

ternary systems, however, will incidentally give a sufficient account of the simpler ones.

Critical solutions: binodal curves and surfaces. Addition of *C* brings about an approach in composition in the two layers, as shown at *d* and *e*, or *f* and *g*. Finally, at a point *c* the two layers become identical; *b* has travelled along the curve *bege* and *a* along *adfc*. The whole curve *begcfda* is commonly termed a 'binodal curve'. Any complex of mean composition represented by a point within the area cut off by it and *ab* will separate into two layers the compositions of which one may represent, as in the diagram, as connected by conjugation lines, or as one sometimes calls them, tie-lines. *c* is a critical point at which the two layers merge into one, and the solution at it is called the 'critical solution' for the temperature considered.

At higher temperatures, if mutual solubility be assumed to increase as temperature rises, the isotherms making up Figure 72 are of similar form, but the length of the binodal curve steadily decreases and ultimately it becomes the point *k*. The curve *ck* connects all the critical points of the intermediate temperatures and is usually termed the 'critical curve': the binodal curves make up the 'binodal surface' *acbk*. *k* is the upper critical point of the system: at all temperatures above it every binary or ternary mixture of the components forms a single liquid phase. The system in Figure 72 shows *k* on the binary surface *ABT*; but of course it may happen that the upper critical point is attained in a ternary, instead of in a binary, mixture. Moreover, since there are binary liquid mixtures which show increasing miscibility as temperature falls, a lower critical temperature in either binary or ternary systems, or both, is also possible. Figure 74 shows

a case where there are upper and lower ternary critical points.

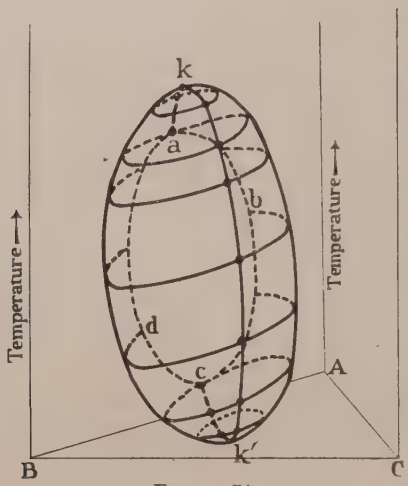


FIGURE 74.

abcd is the binary system on the plane *ABT*, *a* and *c* being the upper and lower binary critical points, respectively. *k* and *k'* are the upper and lower ternary critical points, and *akk'c* is the critical curve. An isotherm between *a* and *k*, or between *c* and *k'*, will have the form shown in Figure 75. Within these temperature ranges the three components are completely miscible in pairs, but ternary systems of compositions falling within a certain area *efgh* resolve themselves into pairs of liquid phases, such as *f* and *g*, shown connected by tie-lines.

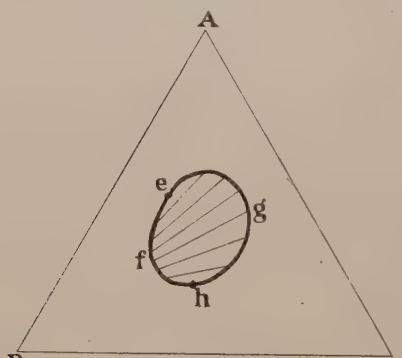


FIGURE 75.

Relations of this kind might even hold for all temperatures in the range of partial miscibility: in such cases there would be, at any one of these temperatures, two critical

solutions, as *e* and *h*, and the complete critical curve would be a closed one.

Applications in quantitative analysis. Two applications of the relations represented in Figures 73 and 74 to analysis of mixtures are well worth noting. Suppose that *B* and *C*, in Figure 76, are miscible in all proportions, and *A* and *C* likewise, but that *A* and *B* are only partially so. The binodal curve for a convenient temperature of working is *acb*. The practical methods of obtaining these curves in the first place must be sought in more detailed text-books.

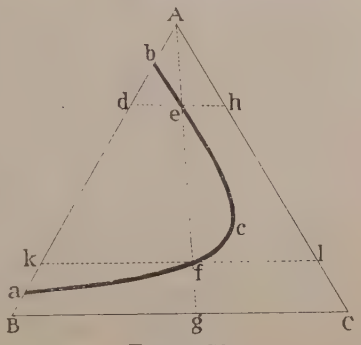


FIGURE 76.

If now an analysis be required of a mixture of *B* and *C* (where, for example, *B* may be water and *C* alcohol) in unknown proportions, the following procedure is possible.

Liquid *A* (toluene, for example) is added gradually to a known weight *W* of the mixture. At first it dissolves completely on shaking. Then a point is reached at which a faint turbidity remains permanently, the amount of *A* which has been added being *W'*. This turbidity is due to the appearance of small particles of a second liquid phase. Addition of more *A* will cause the separation of more of this phase, giving, ultimately, two distinct layers. When the first turbidity appears, the percentage of *A* in the ternary mixture is $\frac{W'}{W+W'} \times 100$, represented, say, by the length *Bk* (or *Cl*) in the figure. The exact composition, therefore, of the mixture must lie somewhere on *kl*, parallel

to *BC*. It must also lie on the binodal curve, since a second liquid phase has occurred. It must then be at the intersection *f*. It follows at once that the composition of the original binary mixture is given by *g*, the point of intersection of the line *Af* produced with the side *BC*. The accuracy of the determination, which is really a titration, may be tested by continuing the addition of *A* until a point is reached at which the two liquid phases again become one. If the percentage of *A* in this final mixture be given by *Bd*, and if *dh*, parallel to *BC*, cut the binodal curve at *e*, then *A*, *e* and *f* must lie on the same straight line.

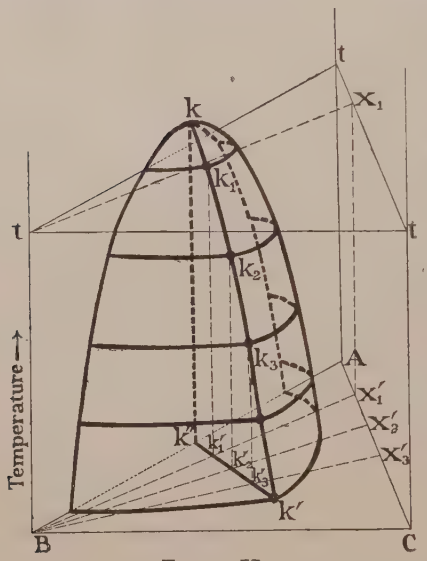


FIGURE 77.

For the analysis of mixtures lying nearer to *C* than the intersection with *BC* of the tangent from *A* to the binodal curve, it is obvious that a known amount of pure *B* must first be added before the titration method can be applied.

A second principle which has been applied for purposes of analysis may be briefly illustrated from such a case as that of Figure 72, which is reproduced, somewhat modified and with additions, in Figure 77. *k* gives

both the temperature and composition of the binary critical solution of A and B. kk' is the ternary critical solution curve when a third component C is introduced. $k''k'$ is the vertical projection of kk' on the base triangle. Only those ternary mixtures having compositions lying along $k''k'$ can have critical solution temperatures. For all others in the heterogeneous area there will be a temperature at which homogeneity occurs, but this will be due to the decrease in amount, and ultimate disappearance, of one of the two layers, not to the merging of finite quantities of the two because of identity of composition; a totally different phenomenon. In the one case the passage is to one end of a tie-line: in the other, the two ends of a tie-line coincide.

Suppose that an impure sample of A contains an unknown proportion of C, which it is desired to determine. Its composition will lie somewhere on AC. Now the temperature t of the critical phenomenon between this mixture and B may be experimentally determined. The procedure will involve progressive additions of B to the mixture until the proportion is reached which at the right temperature gives the characteristic critical change from two layers. The composition of the mixture will obviously lie at that point k_1 where the ternary critical curve cuts the isothermal (t deg.) triangular plane, or, what comes to the same thing, at a point k_1' in the base ($t = 0$) plane which is at a distance t vertically below kk'. If now a horizontal line be drawn from B (or the corresponding point at temperature t) through k_1' (or k_1) and produced, it will cut AC (or the plane ACt) at a point x_1' (or x_1) which gives the previously unknown proportion of C in A. Similarly any other mixture x_2', x_3' may be analysed.

The method is of course quite empirical, since one first

determines kk' for known mixtures of A, B and C, and then uses this knowledge conversely to ascertain unknown concentrations. Its sensitiveness depends upon the sharpness of fall of the curve kk', that is to say, on the magnitude of kk_1 as compared with Ax_1'. In many cases the temperature gradient is very steep indeed, and quite small additions of C to A make large changes in the critical solution temperature.

As a rule the method is applied for the detection of only small proportions of C in A, so that it is necessary for the analyst to know only a part of the ternary critical solution curve. More often than not, investigators simply plot a few alterations in critical solution temperature against the corresponding percentages of C in the A–C mixtures, and use this curve for the interpolations. It is necessary, however, to be cautious when only a partial investigation is made, since in such a case as that of Figure 74 there will be two quite different mixtures of B and A containing C which will give the same critical solution temperature.

The objection to using changes in critical solution temperatures as criteria of purity of one of two components is that they so often do not fall in convenient ranges of temperature. This may be avoided by using a ternary mixture of composition selected to give a critical solution temperature at a convenient point. Such a temperature will similarly be affected by additions of a fourth component as impurity in one of the three, and a relation between the temperature changes and composition may be experimentally established.

Partial miscibility of two pairs of liquid components. Passing now to the general case where at certain temperatures partial miscibility is characteristic of two of the three pairs of liquid components, a couple of space models will

serve as illustrations. The simplest case will be that in which both pairs of partially miscible liquids have upper critical points, and where, at a temperature below both of these, the form of the isotherm will be that of Figure 78, where the two heterogeneous regions are separated from one another, each with its own critical solution *a* or *b*.

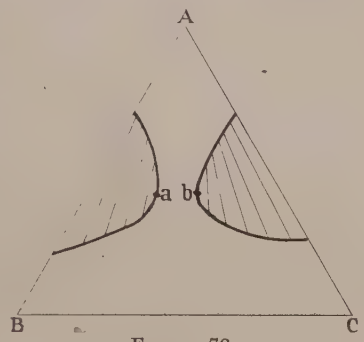


FIGURE 78.

At lower temperatures these regions will become greater: at some point they will touch and then merge into one another giving isotherms like Figure 79, in which there is no longer any critical solution.

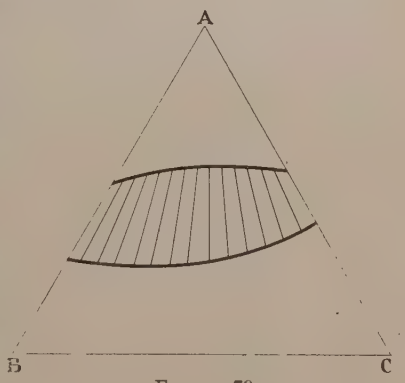


FIGURE 79.

The building of a space (composition-temperature) model for this case does not offer any difficulty.

It may sometimes happen, however, that with rise of temperature the heterogeneous region of Figure 79 does not separate into two distinct parts. This will be the case, for example, if the temperature of the binary critical solution point for *A* and *B* is reached before such separation has occurred. The isotherm at this point will

be as in Figure 80; and thereafter, as temperature rises, as in Figure 81 until heterogeneity ceases.

A typical three-dimensional model including these types

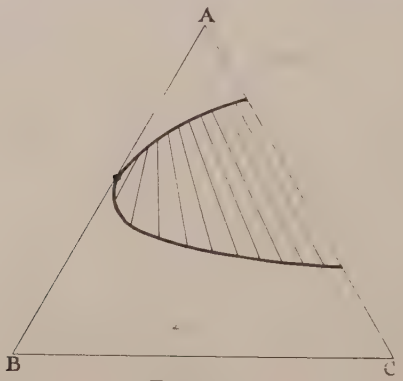


FIGURE 80.

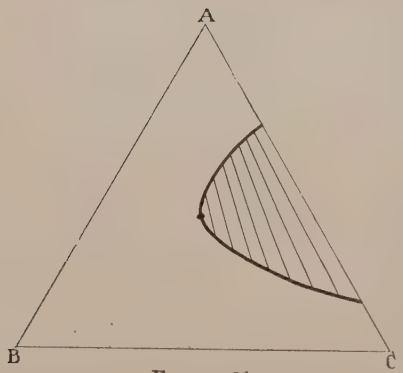


FIGURE 81.

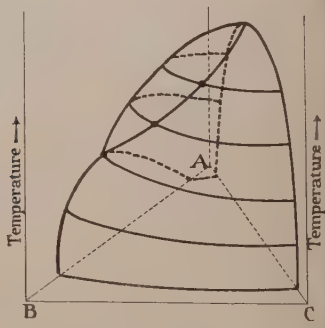


FIGURE 82.

is given in Figure 82. Actually it represents diagrammatically the system water (*A*), phenol (*B*) and aniline (*C*) (Schreinemakers, *Zeit. phys. Chem.*, 1899, **29**, 577 and **30**, 460).

Here the upper critical points are on the respective binary systems, but it is a simple exercise to draw the altered diagram for the case where one or both of the upper points are ternary.

The form of the model when one pair of liquids has an upper and the other a lower critical point may also be noted. Figure 83 gives a representation of the system water (*A*), phenol (*B*) and triethylamine (*C*) which should be readily understood from the previous discussion (Meerburg, *Zeit. phys. Chem.*, 1902, **40**, 641).

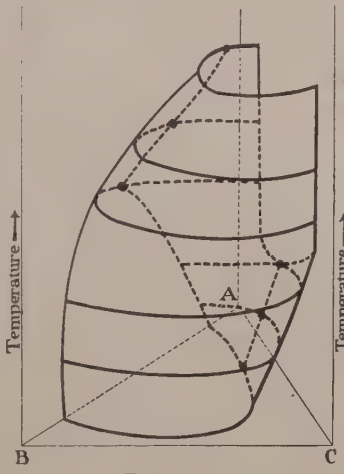


FIGURE 83.

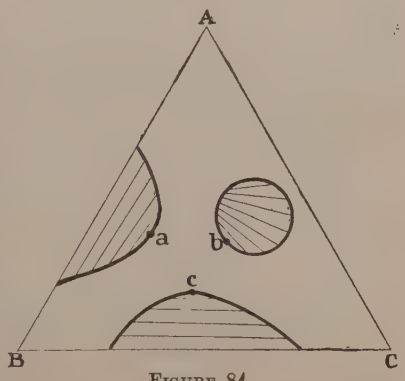


FIGURE 84.

Partial miscibility of three pairs of liquid components. Lastly, one may indicate by a few isotherms some characteristic features of possible systems in which each of the three pairs of liquids may give two liquid phases over certain temperature ranges. It will be assumed that each pair will be completely miscible at some definite upper

temperature. Above the highest of these, therefore, if there be a heterogeneous field, it must be ternary in composition at all points, the isotherm type being that of Figure 75 with two critical points. At lower temperatures, one, two or three two-phase fields may appear, and these may or may not have a binary system as part of the boundary. Examples are shown in Figures 84 and 85. Ultimately, as temperature falls, every field must be bounded by at least one side of the triangle. Then at lower temperatures still, two heterogeneous fields may merge into one, contact first taking place at the respective critical points. Figure 85, for example, would then pass through the forms of Figures 86 and 87, where, in the latter, the third heterogeneous field at its critical point is just in contact with that formed by the merging of the other two.

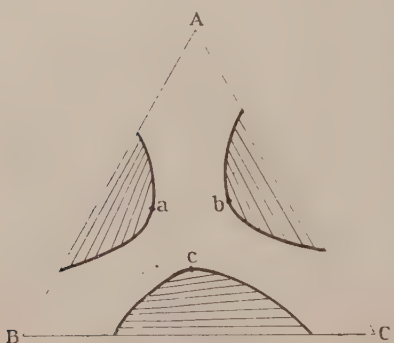


FIGURE 85.

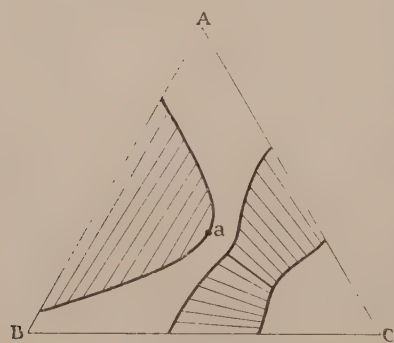


FIGURE 86.

At this temperature it is clear that the critical solution *a* is in equilibrium with another solution *d*. Any further fall

of temperature will now bring the end *a* of the line *da* into contact with one of the tie-lines in the other area, i.e. *a* will now be a mixture which will resolve itself into two phases lying on the binodal curve. This means that solution *d* will be in equilibrium with each of two other liquid phases, which are themselves in equilibrium. Thus we attain a three-layer system, the type of which is shown in Figure 88.

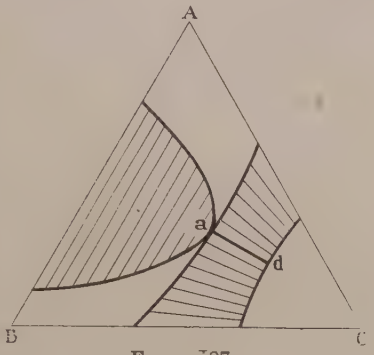


FIGURE 87.

Any complex represented by a point within the triangle *def* will give three liquid phases of compositions *d*, *e* and *f* respectively. The position of such a point will determine the proportions of the components in each layer. Thus, from a quantity of mixture *p*, the fraction *Mp/Mf* will go into the layer of composition *f*: *fp/Mf* will be in the other two layers, and of it *dM/de* will be of composition *e* and *eM/ed* of composition *d*.

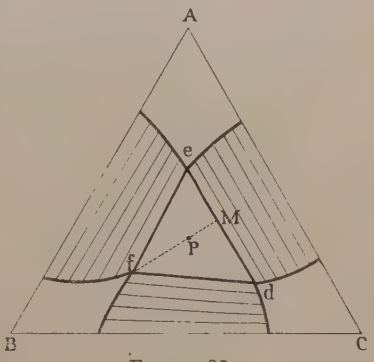


FIGURE 88.

The three areas shown with tie-lines include all complexes giving two liquid phases: the remaining three areas include the unsaturated or homogeneous solutions.

These indications suffice to show the relationships that are possible in such cases. It will be at once apparent that the possible three-dimensional figures may be of rather diverse types according to the natures of the components, and the student should amplify the descriptions of the various types that have been indicated and deduce for himself other possibilities.

The equilibrium type: $AB + CD \rightleftarrows AD + CB$. One special type of three-component system deserves some little attention in conclusion, since for its satisfactory representation one must employ graphical methods, the consideration of which now will facilitate the treatment of four-component systems in the next chapter.

This is a system in which double decomposition may occur between two sets of substances. Important and familiar examples are the hydrolyses of salts and esters. A general chemical equation for reactions of this kind is

$$AB + CD \rightleftarrows AD + CB.$$

It is clear that since the four substances are connected by this equation, the composition of an equilibrium mixture of the four may be expressed in terms of any three; since if, for example, AB, CD and AD are specified, CB is at once known from the equation

$$\frac{AB \times CD}{AD} = k \,.\, CB,$$

where k is the equilibrium constant of the reaction, or the ratio of the backward to the forward velocity.

Or, again, one might express all compositions in terms of the radicals. Thus if a, b, c and d are the weights of the radicals A (+), B (−), C (+) and D (−), respectively, in any mixture, the relative numbers of equivalents, a_e, b_e, c_e and d_e are readily calculated, and since they are present in such proportions that $a_e + c_e$ must always equal $b_e + d_e$, it

follows that the value of any one of them is always known when the values of the three others are specified.

Graphical representation. One cannot in such a case plot compositions of all possible phases in a triangle such as that used hitherto, in which the three components, say AB, CD and AD, are represented by the respective angular points. It is impossible, for example, to plot the compound CB in such a figure. Some different scheme, therefore, must be devised.

Now since in any particular phase the number of equivalents of the positive radicals must equal that of the negative, it follows, if we take this number as unity, that the composition may be expressed as

$$A_{1-y}B_{1-x}C_yD_x.$$

Therefore by plotting x and y as co-ordinates, it should be possible to represent compositions of all phases. Rectangular co-ordinates will give the simplest case, and the way in which the diagram is constructed may be followed by considering Figure 89.

x values are here plotted as abscissae on the axis marked X, and y values as ordinates on that marked Y. If $x = 0$ and $y = 0$, the phase consists solely of the component AB, that is to say, the point of origin represents pure AB. If $x = 1$ and $y = 0$, the phase is pure AD, represented then by a point unit distance from AB along the X axis. Similarly, for $x = 0$ and $y = 1$, we get BC at unit distance upwards on the Y axis. Finally $x = 1$ and $y = 1$, gives CD as shown. Thus the four substances taking part in the double decomposition may be represented by the respective corners of a square.

Any phase which contains two or more of these four substances, and the composition of which is expressed in terms of any three of them arbitrarily selected as

components, may be represented by a point either on the sides of, or within, the square, as the case may be.

As an example, a phase containing a equivalents of AB, b of CD, c of AD and d of BC, which may be written as $A_{a+c}B_{a+d}C_{b+d}D_{b+c}$ is represented by a point p such that

$$y = bp = \frac{b+d}{a+b+c+d}$$

and

$$x = ap = \frac{b+c}{a+b+c+d},$$

since substitution of these values in the above composition reduces it to the general form $A_{1-}B_{1-x}C_yD_x$.

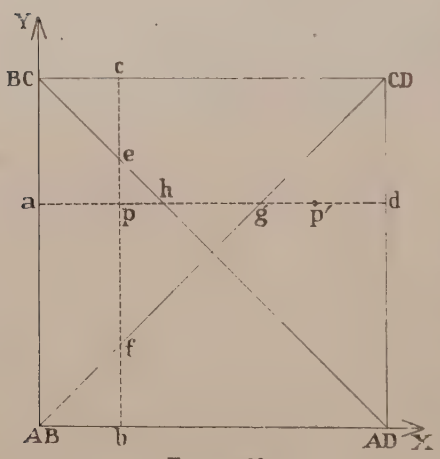


FIGURE 89.

This expression in terms of the radicals is more rational, in the case of solutions, than any attempt at expression in terms of the molecules present, since we have no means of telling exactly how radicals may pair in a solution, nor indeed to what extent they form molecules at all or remain separated as ions. In very dilute solutions only can some approximate idea be formed.

Thus the composition of the point p, in Figure 89, may be expressed not only, as above, in terms of AB, CD, AD and BC, but also as $(1-x-y)AB+yBC+xAD$ or, again, as $(1-y)AB+(y-x)BC+xCD$, since all three

statements give the same relative proportions between the radicals, namely, those of the general formula, $A_{1-y}B_{1-x}C_yD_x$. If, as in this particular case, y be greater than x, the composition cannot be expressed in equivalent proportions of $BC+CD+AD$ or $AB+AD+CD$ without some of these substances appearing in negative amount, which would be meaningless. These facts are immediately obvious from Figure 89, since p, besides falling in the square $AB-AD-CD-BC$, is also within each of the triangles $BC-AB-AD$ and $AB-BC-CD$; but it is outside of both $BC-AD-CD$ and $AB-AD-CD$. Similarly a point p', for which x is greater than y, may represent $BC+CD+AD$ in certain proportions, or $AB+CD+AD$, or all four $AB+AD+CD+BC$, and there is usually no more reason for choosing one set of constituents than the other. To express all compositions in terms of the radicals is therefore the more reasonable method.

Representing the relative numbers of equivalents of the respective radicals by a and c (positive) and b and d (negative) it will be seen that the method really amounts to plotting the ratio

$$\frac{c}{a+c}\,(=y)\text{ against }\frac{d}{b+d}\,(=x).$$

If, however, it be desired for any special reason to express compositions in terms of molecules rather than radicals the proportions may be read just as easily from the figure. Thus while p represents $A_{1-bp}B_{1-ap}C_{bp}D_{ap}$ it also represents ap of AD, bp of BC and pe $(=ph)$ of AB, for, since $ap=ce$, it follows that $ap+bp+pe=1$, the side of the square. Also it represents ap of CD, pc of AB and pf $(=pg)$ of BC, for, since $ap=bf$, $ap+pc+pf=1$.

A typical example. Figure 90 will serve as an illustration of a system plotted in this way. The equilibrium is

$AB + CD = AD + CB$. The possible solid phases represented are CD and a molecular compound K of AB and AD. Such a system approximates to that given by the equilibria at 30° C. between ordinary alcohol, caustic potash, water and potassium ethylate, and one may perhaps most readily appreciate the significance of the respective fields from a consideration of the changes which occur when, say, water (AB) is steadily added to pure potassium ethylate (CD).

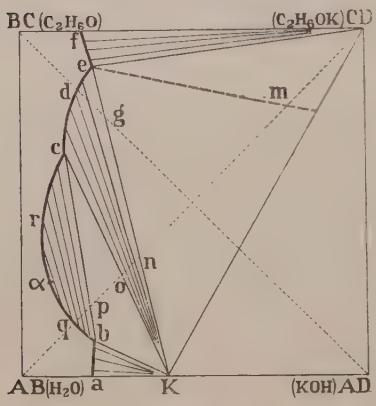


FIGURE 90.

The complexes formed will lie on the line joining CD and AB. Pure ethylate may be in equilibrium with any of the solutions represented on the line ef. Addition of water to it gives a complex falling in the triangle of $e.K.CD$, and this resolves itself into solution e and a mixture of the two solids, namely, ethylate and that with the composition of the point K ($KOH \cdot 2H_2O$). The action is simply hydrolysis; the alcohol produced forms the solution with some of the caustic potash and some of the water, while the rest of the potash and the water form the solid K. For a particular complex m the proportions of solution and respective solids may at once be read from the diagram in the way frequently illustrated in the preceding pages.

Further addition of water leads to a steady decrease of the ethylate, until at n it has all vanished and of the

total complex the fraction nK/eK is solution e and en/eK is solid K. With more water the complexes pass within the triangle ecK from n to o; the solid phase remains the same, K, while the solution changes continuously from e to c. Beyond o, in the triangle cbK, the same solid is present, but there are now two liquid phases in equilibrium, namely, those of compositions c and b respectively. The proportions between the three phases depend only upon the position of the complex along op, and are readily ascertained.

At p the solid phase K vanishes, and the complex consists of the two solutions only, being mainly b: beyond p the compositions of the two layers change along cr and bq, respectively. At q the amount of r is zero and thereafter, from q to AB, the system is single-phase and unsaturated.

The curve $c\alpha b$ is binodal, having a critical point at α where the two layers become identical in composition.

The equilibrium systems given by complexes falling within the various fields may now be summarized. It will be assumed that the pressure has been arbitrarily fixed at a value making the system condensed, that is, without a vapour phase. This means that one degree of freedom has been exercised.

Field $BC.AB.abacef$: one liquid phase: tervariant (isothermal bivariant).

Fields $CD.ef$, Kec, Kba: one liquid and one solid phase: bivariant (isothermal univariant).

Field $c\alpha b$: two liquid phases: ditto.

„ $CD.eK$: two solid and one liquid phase: univariant (isothermal invariant).

In the field $CD.K.AD$ three solid phases can exist, but no liquid.

Of other possible three-component systems it is proposed to discuss only one general type, namely, that in which mixed crystals may be formed by components. For reasons that will there appear, this discussion is postponed to the latter part of Chapter VIII.

CHAPTER VI

FOUR-COMPONENT SYSTEMS

General. It is not proposed to aim at anything approaching a complete treatment even of condensed four-component systems. The possible complexity is naturally much greater than in the lower systems, and the working out of general types on lines similar to those there adopted is still incomplete: nor indeed is much to be gained by what becomes rather mechanical procedure unless specific experimental work leads to it.

With four components and no arbitrary limitations upon any variables, the maximum number of phases which may coexist becomes six, and there are many possibilities as to the states in which the six may be present. There can be only one vapour phase, but there are no limitations theoretically to the grouping of the remaining five as liquids or solids or both. Such a system is invariant. Five phases give a univariant system: four a bivariant system: and so on. Where a degree of freedom is exercised in a choice of pressure or temperature, the variance of the system is correspondingly reduced. This will be so in all cases touched upon here. Thus, as in the previous chapter, the vapour phase will not be considered; that is to say, systems will be regarded as condensed, or subjected to pressures greater than those at

which vapour phases can exist. If in practice one does not trouble actually to maintain this pressure, but works at any convenient value such as that of the atmosphere, the resulting changes in any system will be, as already pointed out in the similar cases of ternary systems, within the limit of ordinary experimental error. In condensed quaternary systems a single phase will be quadrivariant; two phases, tervariant; three, bivariant; four, univariant; five, invariant.

Graphical Representation. Increase of components means increase in the difficulty of adequately representing systems graphically. It has been seen that three independently variable components may be plotted in two dimensions either by means of a triangle or a square. A fourth component can be included only in a three-dimensional figure, so that the isobaric isotherm in four-component systems will be a space model, and one may no longer plot composition and temperature in one figure unless arbitrary limitations be imposed regarding at least one component.

The tetrahedral representation of composition. Any four components *A*, *B*, *C*, *D*, will, when each one of them in turn vanishes in amount, give the four three-component systems, *B–C–D*, *A–C–D*, *A–B–D* and *A–B–C*. In view of the usefulness of the equilateral triangle in representing the latter, it is natural to suggest four triangles, arranged to form a regular tetrahedron, as suitable for plotting isotherms of four components.

In Figure 91, showing a tetrahedron in perspective, the angles *A*, *B*, *C* and *D* represent respective pure components. The six possible binary systems, *A–B*, *A–C*, *A–D*, *B–C*, *B–D* and *C–D*, are given by the lines joining the angular points. The ternary systems will be in the four bounding triangular

surfaces, while one is able to represent every possible quaternary mixture by points in the space enclosed by these.

As before, each side of a triangle may be taken as equal to 100 units, and compositions may be expressed in percentages either by weight or by molecule. If now, through any point P, taken within the tetrahedron, parallels be drawn to the respective edges, meeting the bounding surfaces, four regular tetrahedra will be formed, as indicated in Figure 91, with P as common apex. The lengths of edge in these tetrahedra are Pa, Pb, Pc and Pd, respectively.

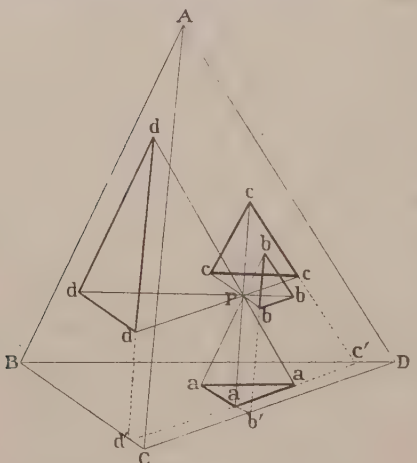


FIGURE 91.

The simple construction of the dotted lines makes it obvious that

$$Pa + Pb + Pc + Pd = aa + ab' + ac' + ad'$$
$$= c'd' + ab' = CD;$$

or, the sum of these distances is equal to the length of edge of the large tetrahedron, 100 units. If then Pa $(= aa)$ be proportional to the percentage of component A, Pb $(= bb)$ to that of B, Pc $(= cc)$ to that of C, and Pd $(= dd)$ to that of D, this quaternary mixture is definitely represented by the point P, and according to the position of such a point, every possible mixture of the components may be similarly represented.

Applications. This method of plotting may be illustrated by applying it to two or three simple general types, selected according to whether a component be classifiable as a solid solute or as a solvent. Following Schreinemakers, the cases chosen will be those where the components are:

I. One solid, *A*, and three liquids, *B*, *C* and *D*.

II. Two solids, *A* and *C*, and two liquids, *B* and *D*.

III. Three solids, *A*, *B* and *C*, and one liquid, *D*.

Further, for the sake of simplicity, it will be assumed that only one liquid phase may exist in each case.

I. *One solid: three liquids.* Those isotherms for case I which hold for temperatures below the melting-point of pure *A* and above the freezing-points of *B*, *C* and *D* will take the form of Figure 92.

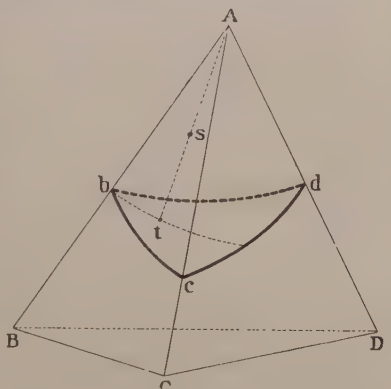


FIGURE 92.

The points *b*, *c* and *d* on the edges *AB*, *AC* and *AD* represent, respectively, the solubilities of *A* in *B*, *C* and *D*. The ternary saturation curves (compare Figure 42, Chapter V) are *bc*, *cd* and *bd*. The quaternary saturation surface is *bcd*.

In every case two phases are present, the system being regarded as condensed, that is, the pressure so chosen that the vapour phase does not appear. There are therefore three degrees of freedom possessed by every two-phase complex in equilibrium: temperature and the concentrations of two components may be varied without either phase disappearing or a new one appearing.

In the space *BCDbcd* all mixtures are unsaturated liquids, single phases. Single liquid phases of compositions in *Abcd* would be supersaturated and separate into solid *A* and a liquid on the surface *bcd*. Thus the complex *s* would give the proportion *st*/*At* as solid *A* and *As*/*At* as liquid of the composition *t*. The number of phase regions into which the tetrahedron is divided in this very simple case is thus two.

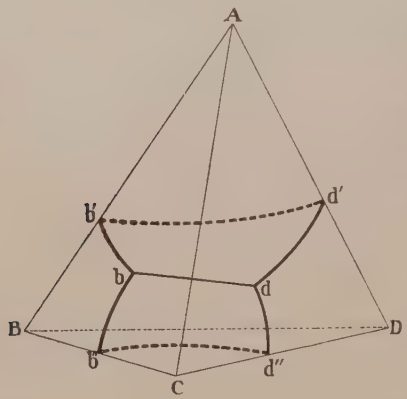


FIGURE 93.

II. *Two solids: two liquids.* For case II, where *A* and *C* are solids and *B* and *D* are liquids, the isotherm takes the form of Figure 93.

Two of the ternary systems, namely, *ABD* and *CBD*, are of the same kind as were all four in Figure 92, each giving a single curve (*b'd'* or *b''d''*) of solutions in equilibrium with a solid (*A* or *C*). In the remaining two, *ABC* and *ACD*, where in each case there are two solid solutes and one liquid, two intersecting curves are given, similar in type to the right-hand portion of Figure 44 in Chapter V. Thus along *b'b* the solutions are in equilibrium with solid *A*; along *b''b* with solid *C*. At *b* the solution and the two solids, *A* and *C*, coexist. Similarly with solution *d* the same two solids are in equilibrium. In their respective ternary systems, *b* and *d* are (condensed) univariant points: alteration of temperature will not reduce or increase the number of phases. In the

quaternary system they are bivariant points. Temperature being fixed they become univariant; the composition of the liquid phase may then be altered by addition of another component and one obtains a curve *bd* giving quaternary solutions in equilibrium with solid *A* and solid *C*.

There are now two saturation surfaces; points on the one, *b'bdd'*, are in equilibrium with *A*; on the other, *b''bdd''*, with *C*. The space behind these surfaces includes, as single phases, all unsaturated solutions. The space in front includes mixtures which will separate into two or more phases, and it consists of three distinct portions. Of these, the first is bounded by the five surfaces *Ab'd'*, *Ab'b*, *Abd*, *Ad'd* and *bdd'b*; all complexes represented within it will give solid *A* and a solution on the last-mentioned surface. The second is similar. It is bounded by *Cb''d''*, *Cb''b*, *Cbd*, *Cdd''* and *bdb''d''*; complexes within it resolve themselves into solid *C* and a solution on this last surface. The third is different. It includes the remainder of the upper space and is bounded by the four triangular surfaces *ACb*, *ACd*, *Abd* and *Cbd*. Complexes falling within it give two solid phases, *A* and *C*, and a solution lying on the line *bd*.

III. *Three solids: one liquid.* The third case, where *A*, *B* and *C* are solids and *D* is a liquid solvent, gives rise to isotherms such as Figure 94.

The resemblance to Figure 41, Chapter V, is quite marked. In that case formation of liquid solutions from three solids was brought about by rise of temperature: in this case it is effected by addition of a fourth (liquid) component in which all three solids are assumed to be soluble. *a*, *b* and *c* give the respective solubilities of *A*, *B* and *C* in *D*. In each ternary system there are two curves meet-

ing at a point where two solids and a solution coexist. The pairs of curves are:

ad and *bd* in the system *A–B–D*;
be and *ec* in the system *B–C–D*;
cf and *af* in the system *A–C–D*.

In the quaternary system are three curves, *dg*, *eg* and *fg*, along each of which a pair of solid components and a solution are in equilibrium. These three curves meet at the point *g*, where there is a solution saturated with *A*, *B* and *C*. This will be an (isothermal, condensed) invariant system. The position of *g* will vary with temperature, but at a selected temperature the three solids cannot be in equilibrium with any other solution than that of composition *g*.

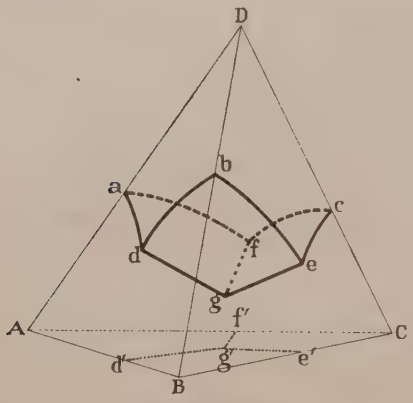


FIGURE 94.

There are, thus, at the selected temperature and pressure of Figure 94, seven invariant saturation points of which one (*g*) is four-phase quaternary, three (*d*, *e*, *f*) are three-phase ternary, and three (*a*, *b*, *c*) are two-phase binary. Also, there are nine univariant saturation curves of which three (*dg*, *eg*, *fg*) are three-phase quaternary and the remaining six (*ad*, *bd*, *be*, *ce*, *cf*, *af*) are two-phase ternary: and there are three bivariant saturation surfaces (*bdge*, *cegf* and *afgd*), all of which are two-phase quaternary.

In the space lying above these surfaces and extending to

pure solvent *D*, only a single phase, unsaturated liquid, can exist. In it, therefore, the system is tervariant.

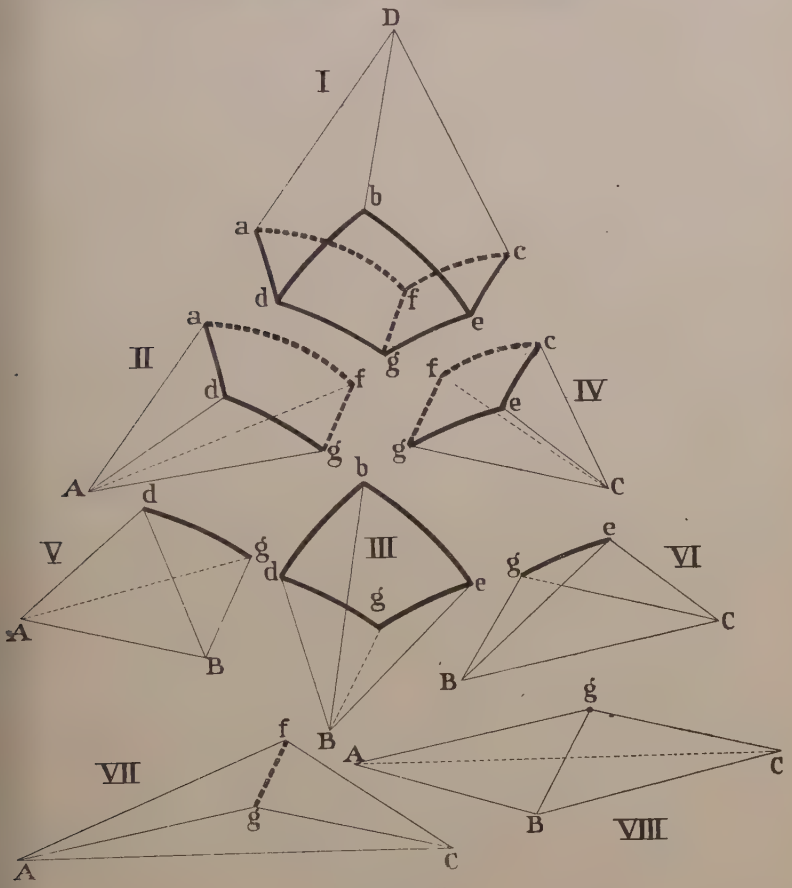


FIGURE 95.

The portion of the tetrahedron lying below these saturation surfaces is polyphase, and there are seven distinct sections in it. The boundaries of these various regions

may be followed from Figure 94, while in Figure 95 the several portions of the tetrahedron are represented separately, the lettering showing quite clearly how the parts fit together to form the whole model.

System No. I, tervariant, single-phase, requires no further description. No. II is bivariant, the two phases being solid *A* and a solution lying on the surface *adgf*. Its bounding faces, other than the saturation surface, will be traced out by a straight rod (or line) of adjustable length with one end pivoted on *A* while the other travels round the edges of this saturation surface. III and IV are similar. V is univariant, the three phases being solid *A*, solid *B* and a solution lying somewhere on the curve *dg*. This region may be described as 'double-gabled', the gables being *dg* and *AB*, and the bounding surfaces being the three triangular planes *Adg*, *ABg* and *Bdg*. VI and VII are similar. Region VIII is invariant, or four-phase, three solids *A*, *B* and *C* coexisting with solution of composition *g*. *g* is its apex, the triangle *ABC* is its base, and its other three walls are *ABg*, *BCg* and *ACg*.

It is on these various regions that attention should be focused. It is a mistake to attend too exclusively to the saturation surfaces, curves and points. These are boundaries and important as such, but the essential matters are the regions which they bound.

Projections of the tetrahedron. In simple cases, such as these three, a perspective drawing of the tetrahedron is readily made and serves to show clearly the different divisions. To make it more than qualitative, however, is difficult: accurate plotting in a perspective drawing is not easy. It is therefore preferable in practice to work with projections on which plotting may be carried out readily and accurately. If two projections in different

directions be given, the space model may always be reconstructed.

Of the possible projections, those made orthogonally, that is to say, at right angles, to selected planes are by far the most useful. A perspective projection, on the other hand, may give almost nothing at all, as for example that from one of the angles of the tetrahedron to the opposite triangular surface in a case like that of Figure 92: while in such a case as Figure 94 it will give from D only the three curves $d'g'$, $e'g'$ and $f'g'$ shown dotted in the triangle ABC.

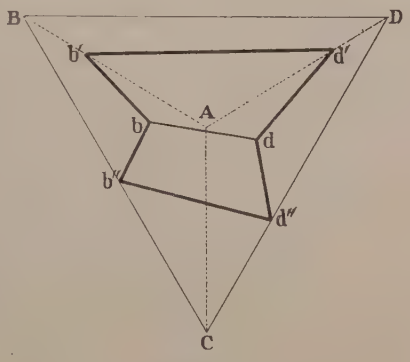


FIGURE 96.

Two orthogonal projections are commonly used. The first is at right angles to any of the four three-sided planes bounding the tetrahedron. The second is at right angles to a plane drawn parallel to two sides of the tetrahedron which do not intersect one another. In Figure 96 is given as an example a projection of Figure 93 by the first method on to the plane BCD.

The lettering is the same as in Figure 93, and a comparison with it will make the relations clear without further words.

The second method gives Figure 97 for the projection of Figure 93 orthogonally on to a plane parallel to both AC and BD, two edges which do not intersect.

The six edges of the tetrahedron give four sides of a square and two diagonals. In the figure the latter are AC

and, BD and their lengths are the same as in the model projected. The similarity to the original figure is greater in the second projection than in the first, and consequently it is usually preferred in practice.

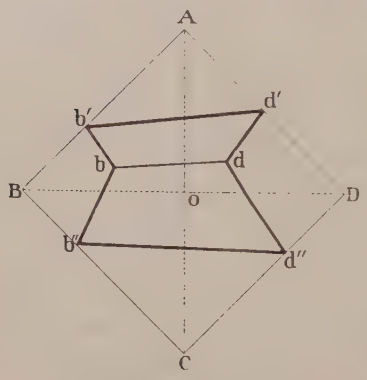


FIGURE 97.

To plot the projection p' of any point p is a simple matter. If p contains a units of A, b of B, c of C, and d of D, so that $a+b+c+d=100$ units $= BD$ or AC, and if we regard BD and AC as axes X and Y, respectively, and take o as the point of origin so that oD and oA (each 50 units) are in positive directions and oB and oC are in negative, then for the point p', $X=\frac{d-b}{2}$ and $Y=\frac{a-c}{2}$; hence the point may be plotted when a, b, c and d are known.

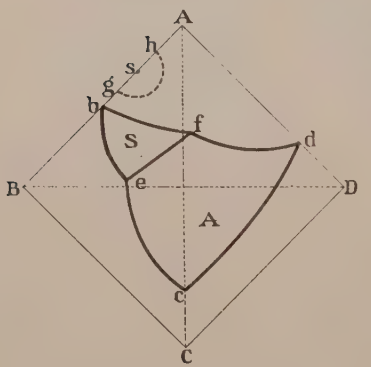


FIGURE 98.

Formation of compounds between components. The student of four-component systems should now proceed to introduce into Figures 92, 93 and 94, or their projections, the necessary modifications which follow when one or more compounds may be formed between components. It is not proposed to do more here than show,

in illustration, the alteration that follows in the simple case of Figure 92 if the solid *A* be able to form a compound (*S*) with the liquid *B*. The projection is given in Figure 98, where *s* gives the composition of the compound A_xB_y.

The ternary system *ABC* has now two curves: *be* gives solutions in equilibrium with solid *S*, and *ec* those with solid *A*. Similarly, in the system *ABD*, there are two

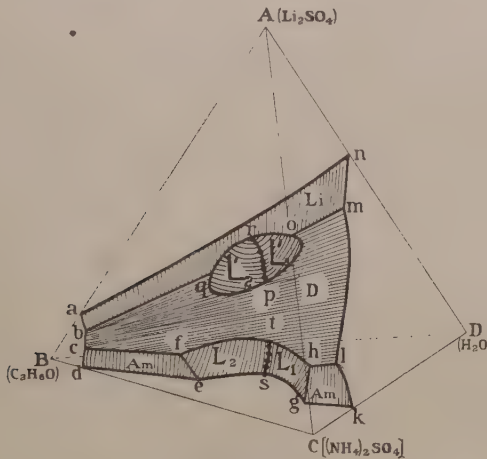


FIGURE 99.

corresponding curves, *bf* and *fd*. In *ACD* there remains as before only the one curve *cd*.

Before the stage of this isotherm is reached, the region of existence of the compound may, of course, be confined to an area such as that between the dotted curve *gh* and the side *AB*.

Appearance of two liquid layers. When two liquid phases appear the number of quaternary surfaces may be largely increased. Again one case by way of illustration must suffice. Figure 99 represents a perspective view of a tetra-

hedral isotherm for a system of components of which B and D are liquids (solvents) and A and C are solids. It is based somewhat upon one of Schreinemakers's * isotherms for the system lithium sulphate (A)-alcohol (B)-ammonium sulphate (C)-water (D), omitting the hydrate of A and exaggerating the solubilities of the salts in B.

The ternary systems A–B–C and A–D–C are of the type shown in the left-hand part of Figure 49, Chapter V. *ab* and *mn*, in the respective systems, give solutions in equilibrium with solid A; *bc* and *ml* those with a compound of A and C, say A_xC_y; *cd* and *lk* those with solid C. The third system A–B–D is of the simplest type with a single curve *an* of solutions coexisting with solid A; while the fourth ternary system, B–C–D, shows two liquid layers and is of the type already represented in Figure 63 of Chapter V. *de* and *gk* are both curves of solutions saturated with solid C, the liquids *e* and *g* being in equilibrium with one another. The binodal curve is *esg*, and *s* is its critical point.

The quaternary saturation surfaces, curves and points are apparent in the figure. All quaternary solutions lying on *abqomn* will coexist with solid A: all on *bcfthlmopqb* with the compound of A and C: all on either area *cdef* or *hgkl* with solid C. *fesght* is a binodal surface, and a liquid of composition corresponding with any point in L_1 will be in equilibrium with some other liquid represented by a point in L_2. The tie-lines between such liquid layers are not shown in the figure; but the points at which the two layers become identical lie along a critical curve *st*. Finally, there is the surface *qropq*, similarly binodal, with a critical curve *rp*. This area lies wholly within the tetrahedron, no point on it being on any of the bounding ternary systems. Two-phase equilibria are characteristic

* *Zeit. phys. Chem.*, 1907, 59, 653.

of all these surfaces, which are, therefore, (isothermal, condensed) bivariant.

On the quaternary boundary lines common to any two fields, three phases will coexist, the systems being univariant. The details may best be given as a table:

Curves.	*Coexisting phases.*
bq and *om*	Solution, solid A and solid A_xB_y.
qro	Two solutions and solid A, the two solutions becoming identical at *r*.
qpo	Two solutions and solid A_xC_y, the solutions becoming identical at *p*.
cf and *hl*	Solution, solid A_xC_y and solid C.
fth	Two solutions (becoming identical at *t*) and solid A_xC_y.
fe and *gh*	Two solutions and solid C.

Lastly, the solution represented at the quaternary point *o* may exist in equilibrium with that at *q* and with the two solids A and A_xB_y. Similarly for solutions at *f* and *h* and the solids C and A_xB_y. Such four-phase systems are invariant when pressure and temperature are fixed.

All points lying underneath these surfaces represent unsaturated solutions. The resolution of the space above them into divisions of which the various surfaces and lines are boundaries, will offer to the student an exercise the solution of which may be based on the same lines as those adopted above in the very much simpler case of Figure 94.

Salt double decomposition in a solvent. The majority of the experimental investigations on four-component systems, which have so far been carried out, have dealt with systems in which one component has been water and the others salts. These belong to the class of most importance in the technical branch generally termed 'salt chemistry'. It is,

indeed, almost solely in this section of technical work that the value of the study of heterogeneous equilibria from the systematic standpoint of the phase rule has been realized and its results applied in the devising of processes: though there is little doubt that in the separations involved in the manufacture of organic products as well, proper scientific procedure must be based on similar studies.

Certain salt equilibria may differ somewhat from other cases in consequence of the possibilities resulting from double decomposition or exchange of radicals. It has already been seen, at the end of the previous chapter, that in three-component systems where reaction of the kind is possible, the triangle is no longer suitable for graphical representation. So in the present systems, the regular tetrahedron ceases to be satisfactory when it is necessary to plot the relations between four components, three of which are connected by the equation

$$AB + CD \rightleftharpoons AD + CB.$$

For if AB, CD, AD and solvent be the components represented at the angles of the tetrahedron, it is not possible to represent a composition CB within the bounds of the figure. But one may deduce from the tetrahedral method a satisfactory representation which at once recalls Figure 89 in Chapter V. The deduction is instructive and worth following.

Deduction of method of representation. Take first the ternary system $AB + CD \rightleftharpoons AD + CB$, and represent each phase in terms of the radicals A', B', C', D', the amounts in any particular phase being w, x, y and z equivalents respectively. Assume for the moment that these radicals are independent variables and form a quaternary system. They may then be represented by the respective angles of a tetrahedron. If this tetrahedron $A'B'C'D'$ be projected

on the plane parallel to AC and BD one obtains the square $A'B'C'D'$ of Figure 100, the four sides and two diagonals being the projections of the six edges of the tetrahedron.

If now the length of each side of the tetrahedron, that is, $w+x+y+z$, be taken equal to 2 (or 200), then in the projection the diagonals $A'C'$ and $B'D' = 2$ (or 200), and if they intersect at O, $OA' = OB' = OC' = OD' = 1$ (or 100).

The four salts AB, BC, CD and AD are then compounds of the components and lie at the middles of the sides of the square $A'B'C'D'$. The point p will now represent the phase $A_wB_xC_yD_z$ if, in the construction set out in Figure 100,

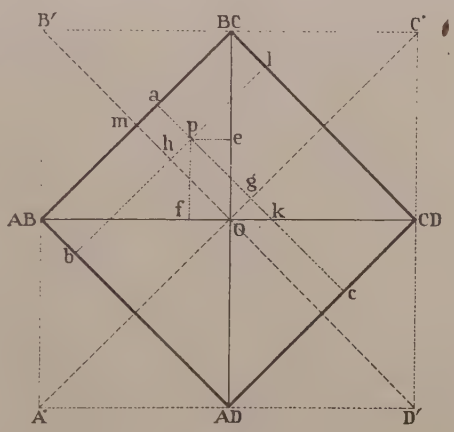


FIGURE 100.

$$pg = \frac{x-z}{2} \quad \text{and} \quad ph = \frac{y-w}{2}.$$

A consideration of Figure 91 and its relation to the orthogonal projection here used will at once show this to be the case, as has also been pointed out in discussing Figure 97. Similarly, all possible combinations of A', B', C' and D', considered as independent variables and without restrictions consequent upon their positive and negative characters, may be represented by points in the square $A'B'C'D'$.

If, however, there be a relation between the components such as exists when two are positive and two are negative radicals, as in a reciprocal salt pair, and therefore $w+y=x+z=1$, it follows that all possible phases must lie in the square $AB.BC.CD.AD$; for complexes lying without it will not contain the necessary equality of positive and negative radicals. Thus a point in the triangle $AB.BC.B'$ represents an impossible mixture of two salts AB and BC with uncombined radical B'. Moreover, this relation between radicals reduces the number of independent components to three.

Drawing the diagonals $BC.AD$ and $AB.CD$, one obtains four triangles, $AB.BC.AD$, $BC.AD.CD$, $CD.BC.AB$ and $AB.AD.CD$, and it is a simple geometrical exercise to show that p represents the same composition whether considered as a point in one of these triangles or as a point in the square $A'B'C'D'$. For example, in the triangle $AB.BC.CD$, p represents

$$pa \text{ equiv. of } CD+pk \text{ of } BC+pl \text{ of } AB.$$

where $$pa+pk+pl=AB.BC=\tfrac{1}{2}A'C'=1.$$

This means that $w=pl$, $x=pk+pl$, $y=pa+pk$ and $z=pa$,

whence $$\frac{x-z}{2}=\frac{pk+pl-pa}{2}=\frac{1-2pa}{2}=pg,$$

and $$\frac{y-w}{2}=\frac{pa+pk-pl}{2}=\frac{1-2pl}{2}=ph,$$

and these are the conditions that p should represent $A_wB_xC_yD_z$ in the projection square $A'B'C'D'$. So for the other triangles.

Next consider the following simplification. First note that $$pe=\tfrac{1}{2}(1-pa-pb)\sqrt{2} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and $$pf=\tfrac{1}{2}(pb-pa)\sqrt{2} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Expressing p in terms of AB, BC and AD, we have present

$$pa \text{ equiv. of } AD+pb \text{ of } BC+(1-ap-bp) \text{ of } AB,$$

or if a phase of this composition contain all the four possible salts of the equilibrium $AB + CD \rightleftarrows BC + AD$, there will be $(ap - n)$ equiv. of AD, $(pb - n)$ of BC, $(1 - ap - bp + n)$ of AB, and n of CD. Putting

$$1 - ap - bp = \text{equiv. } AB - \text{equiv. } CD$$

and $$pb - pa = \text{equiv. } BC - \text{equiv. } AD,$$

it follows from (1) and (2) that

$$pe = \tfrac{1}{2}(\text{equiv. } AB - \text{equiv. } CD)\sqrt{2} \quad . \quad . \quad (3)$$

and $$pf = \tfrac{1}{2}(\text{equiv. } BC - \text{equiv. } AD)\sqrt{2} \quad . \quad . \quad (4)$$

But $A'C' = B'D' = 2$; therefore each half-diagonal $O.AB$, $O.BC$, $O.CD$ and $O.AD$ must equal $\frac{1}{2}\sqrt{2}$.

If, then, one chooses to put $O.AB = O.BC = \&c. = 1$ instead of $\frac{1}{2}\sqrt{2}$, equations (3) and (4) change to

$$pe = \text{equiv. } AB - \text{equiv. } CD$$

and $$pf = \text{equiv. } BC - \text{equiv. } AD,$$

and one obtains the following simplified method of graphically representing the reciprocal salt pair system:

Take two axes bisecting one another at right angles at O and each equal to length 2. Taking directions $O.BC$ and $O.CD$ (Figure 91) as positive, and $O.AB$ and $O.AD$ as negative, plot along the one axis from O, as origin, the difference in equivalent proportions of BC and AD and along the other of AB and CD, the sum of these four molecular proportions being unity: or, briefly, taking bisecting axes each = 200, plot the differences in percentages of equivalents of the respective pairs.

We thus have in Figure 100 three different methods of plotting the composition of a phase, each method giving the same point p. The third method is the one which will be used. To represent the fourth component water, or other solvent, it is now only necessary to take a new axis OW at right angles to the square at O. Putting $OW = O.AB = \&c. = 100$, and plotting the molecular per-

centage of water upwards, W becomes the point representing pure water, and all mixtures of the four components must lie in the pyramid $W.AB.BC.CD.AD$.

As two-dimensional projection, that made orthogonally to the ground plane $AB.BC.CD.AD$ may be taken, and from this and a second projection, say that on the plane $W.AB.CD$, the solid pyramidal diagram may be reconstructed. It goes without saying that from a projection one cannot read directly the compositions of phases. For example, the point O in Figure 100 represents either pure water or any solution whatever in which BC and AD (or AB and CD) are present in equivalent proportions.

Example of pyramidal model. The simplest possible reciprocal salt pair system is that in which neither hydrates nor double salts are formed. Figure 101 represents in perspective the space model of a possible system of this kind at a particular temperature, and its orthogonal projection on the base of the pyramid, while this projection is shown in direct view in Figure 102.

The description of Figure 101 (and its projection) offers little that is new, but the case is so important that it is advisable to go briefly into the dissection of the pyramid. If the case of Figure 94 has been followed, that of Figure 101 will not offer difficulty.

The edges of the pyramid and the diagonals of the base give all the possible binary systems, ten in all. We are concerned only with the four in which, at the temperature of the figure, a liquid phase can appear, namely, those running from the apex (water) to each corner of the base. a, c, e and g give saturated solutions of the respective single salts in water, condensed isothermal binary systems. The four triangles having water at their common apex contain the ternary systems, each assumed to be of the

type of the right-hand portion of Figure 44, Chapter V. *b*, *h*, *f* and *d* are the three-phase ternary systems, invariant under the conditions laid down.

The entry of a third salt to each of the ternary systems adds a degree of freedom and brings all solutions to the

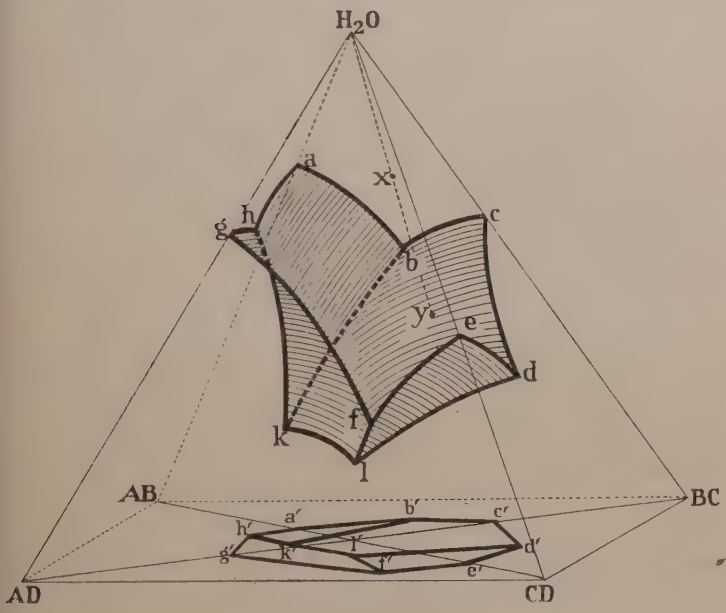


FIGURE 101.

interior of the pyramid: quaternary saturation curves run from each of the three-phase ternary points. Those from *b* and *h* are represented as meeting at *k*, where therefore four phases (solution and the three salts *AD*, *AB* and *BC*) coexist, a quaternary (isothermal, condensed) invariant point. Those from *d* and *f* meet at *l*, a solution saturated simultaneously with respect to *BC*, *CD* and *AD*. Any

attempt to alter the composition of k or l, by dissolving CD or AB as the case may be, will result in one of the solid phases disappearing, namely, AB from the system at k and CD from that at l. There is therefore another saturation curve running between k and l giving solutions saturated with respect to two solids only, BC and AD.

These various curves are the boundaries of four saturation surfaces. Any point on the surface *habkh* represents the composition of a solution saturated with respect to AB; on *ghklfg* with respect to AD; on *eflde* to CD; on *cbkldc* to BC. With these known, it is possible at once to divide the pyramid into sections according to the nature and number of the phases into which complexes of mean composition falling within such sections will resolve themselves.

There are twelve of these sections. The first and most obvious one is that lying between the apex and the four saturation surfaces. All mixtures in this give unsaturated solutions. Such single-phase systems are tervariant when two degrees of freedom have been exercised in fixing temperature and pressure. Concentrations of three components may be varied, within limits, without a new phase appearing. The remaining eleven are below these surfaces and are of three types. Of the first type there are four, of the second five, of the third two.

An example of the first type is that region which is bounded by the area *habk* and the trace of a straight rod (or line) of adjustable length moving with one end on the angle AB as a pivot while the other end passes round the boundary of the area just cited. Any complex in this resolves itself into two phases, solid AB and a solution on the saturation surface. The system is (isothermal, condensed) bivariant. The other three of this type may be

similarly described with respect to the remaining saturation surfaces and their corresponding solids.

To the second type, the term 'double-gabled' may again be applied. An example is the region in which hk and $AD.AB$ are the gables, and the bounding surfaces are the four triangles $h.AD.AB$, $k.AD.AB$, $h.AD.k$ and $h.AB.k$. Complexes in it yield two solids, AD and AB, and a solution of composition somewhere on hk, saturated with both. The condensed systems are univariant at a fixed temperature. The concentration of one component in the system may be varied, within limits, without altering the phase equilibrium. The other divisions of this type have, as their pairs of gables, bk and $AB.BC$, dl and $CD.BC$, fl and $AD.CD$, and kl and $AD.BC$, respectively.

Two examples of the third type divide the remainder of the pyramid. One has an apex at k and its base is the triangle $AB.AD.BC$: its sides are the three triangles $k.AB.AD$, $k.AB.BC$ and $k.AD.BC$. The other has l as apex, $AD.BC.CD$ as triangular base, and corresponding triangular sides. Complexes in either of these give a solution, k or l, as the case may be, and three solids. They are (isothermal, condensed) invariant systems.

It is clear now that one can predict from this three-dimensional isotherm precisely into what phases any possible mixture of components will resolve itself. At other temperatures the division of the model between the various systems of phases may be quite different. That which lies in one type of system at one temperature may lie in an entirely different one at another. From its equilibrium with a solution of given composition it may be possible to remove a certain component at one temperature, while below or above this quite another may separate out. Nor is variation of temperature the only method by which one

may pass from one system to another; obviously this may be done by suitable additions, or removals, of, say, the component water; or by both means together. It is in this way that one may use these systematic investigations for the devising of technical processes for the production of solid salts (*AB* and *CD*, say) by double decomposition between two others (*AC* and *AD*) in presence of a solvent.

Looking now at Figure 102, the projection of

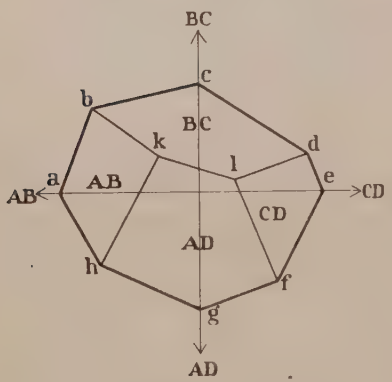


FIGURE 102.

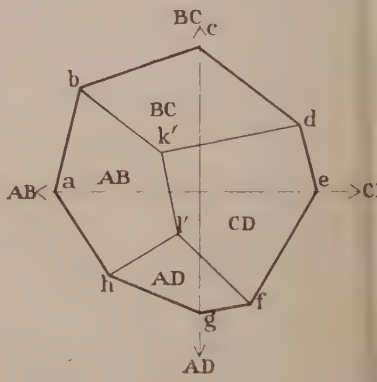


FIGURE 103.

Figure 101, it is quite apparent that there may be another relative division of the plane, namely, that shown in Figure 103.

In this case, before the curves from *b* and *h* meet at *k*, a new phase, solid *CD*, separates out at *k′* and *l′*, respectively. The difference between the system of Figure 102 and this one is that in the former *BC* and *AD* can coexist with a series of solutions (along *kl*), while *AB* and *CD* cannot coexist as solids with any solution, whereas, in Figure 103, *AB* and *CD* can, while *BC* and *AD* cannot, coexist with solutions.

The (condensed) invariant point. Now whether the one case or the other will be realized in practice will depend first of all upon the natures of the salts, but secondly upon the variables temperature and pressure, or what is not shown in the projection, water content. The effect of pressure is usually very slight, at any rate within the limits of pressures so far realized experimentally, but temperature may modify these diagrams considerably, so that the isotherms above a certain point may be of the one type, and below it of the other. At that particular point k and l or k' and l' coincide, and the relations are those of Figure 104.

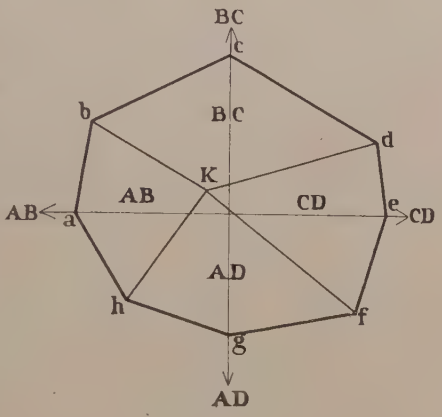


FIGURE 104.

This point of coincidence (K) is a five-phase (four solids and solution), or condensed invariant, system. It can exist only at one specific value for temperature and for each of the concentration variables, so long as the selected constant pressure is maintained. One phase or another disappears if a persistent attempt be made to alter one of these.

Course of isothermal evaporation. It is a simple matter to follow out from a model like Figure 101 the course of isothermal evaporation of an unsaturated solution. Thus a quaternary solution x will, on loss of water, travel along the line $H_2O \,.\, x$ produced until it meets one of the surfaces

at, say, *y*. Here solid (*BC*) will begin to separate. With further evaporation and formation of *BC*, the solution composition moves across this surface, along what may be termed an evaporation line, until a boundary surface *ld*, say, is reached, when a second solid (*CD*) begins to deposit as well: further change would then be along this line to a point (*l*) where three solids (*BC*, *CD* and *AB*) would

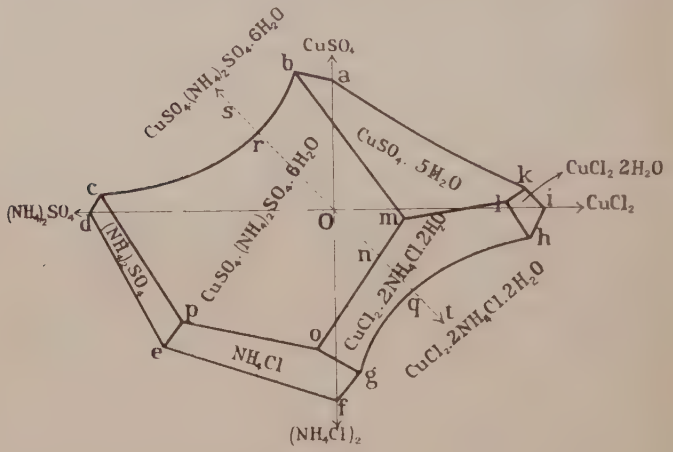


FIGURE 105.

separate. The solution would finally vanish at this point, which is sometimes termed a 'drying-up point'.

Example in which components form compounds. When hydrates (or in general, solvates) and double salts may be formed, the model naturally becomes more complicated, but the complication consists only in greater numbers of the systems illustrated above and not in the addition of anything new. The projection of rather an interesting example is reproduced in Figure 105. The reciprocal salt pair is $CuSO_4 - (NH_4Cl)_2 - (NH_4)_2SO_4 - CuCl_2$ and the solvent is

water. The relations are for 30° C., and the figure is from a paper by Schreinemakers (*Zeit. phys. Chem.*, 1909, **69**, 557).

The significance of the various surfaces, curves and points should be at once apparent with the aid of the formulae entered on the figure. Instead of the four isothermal, condensed, bivariant, quaternary areas of Figure 101, there are here six: instead of the two invariant points *k* and *l*, there are four, namely, *p*, *o*, *m* and *l*. It will be noticed that neither copper sulphate pentahydrate and ammonium chloride, on the one hand, nor copper chloride hydrate and ammonium sulphate, on the other, can exist in equilibrium with one another and a common solution.

A point worth attention is the relation between water and the double salts, $CuSO_4 . (NH_4)_2SO_4 . 6H_2O$ and $CuCl_2 . 2NH_4Cl . 2H_2O$. The two parts, *sO* and *Ot*, of the straight line *st* give the projection of the lines joining the compositions of these salts, respectively, to the apex of the pyramid, which is pure water. It cuts *cb*, the curve along which solutions are in equilibrium with the first double salt, at *r*, and similarly *gh* at *q*. This means that each of these double salts dissolves in water without decomposition. Moreover it is clear that a ternary system is possible in which the components are water, $CuSO_4 . (NH_4)_2SO_4 . 6H_2O$ and $CuCl_2 . 2NH_4Cl . 2H_2O$. The isotherm will consist of two curves, one made up of solutions projected along *rn*, and the other of those projected along *qn*. At *n*, where the curvature changes sharply, both double salts coexist with the same solution.

Determination of solid phases. The determination of the solid phase in contact with any solution may be carried out by adopting precisely the same principle as that described in the chapter on ternary systems. The compositions of

solution, wet residue (solid with adhering solution) and pure solid or mixture of solids, will lie on a straight line, and the application of this fact to determine the latter differs in this case only in that the line runs through a three-dimensional figure instead of on a plane surface.

Common modifications of the method of representation. As many workers on reciprocal salt pairs prefer to modify slightly this pyramidal method of representation, it is advisable to mention the changes they introduce. Instead of expressing compositions as (equivalent) molecular percentages of the respective four salts and the solvent, they express them in terms of the numbers of molecules of the salts present with a fixed number, usually 1,000, of molecules of solvent. The differences between the molecular proportions of *BC* and *AD* are, as before, plotted against those of *AB* and *CD*, and then vertically to each such point is plotted the total sum of the salt molecules of all kinds present. Any point so obtained is of course quite unambiguous.

Further, for convenience, it is usual to decide arbitrarily that *BC* and *AD*, or *AB* and *CD*, shall be regarded as not occurring together in solution, or as being 'incompatible' as solutes, and therefore to tabulate all salt mixtures in any solution in terms of *AB*, *BC* and *CD*, or *AB*, *AD* and *CD* (or in the corresponding sets of three if *AB* and *CD* be selected). This does not affect the position of a point representing the composition of a phase.

Some good examples of diagrams obtained in this way will be found in papers by Hillebrand * and Blasdale † recently published. In the space model built in accordance with this modified method, solutions will of course lie below

* *Journ. Indust. and Eng. Chem.*, 1918, 10, 96.
† Ibid., p. 344.

the surfaces, lines and points of the saturated solutions, not above them as in the pyramidal model. Perhaps this method is a little simpler in some respects, but the advantage, if any, is slight in practice, and there is no advantage at all from a student's point of view.

Other workers, particularly Jänecke (*Gesättigte Salzlösungen*, Kapitel X), make use of the mode of representation for three components shown in Figures 89 and 90 of Chapter V. It has been seen (p. 141) that this amounts to plotting the ratio of one of the positive radicals to the sum of the two against a similar ratio for the negative radicals. The fourth component is then plotted upwards either as a percentage or as the amount present for a given total number of molecules of salt. The method offers no particular advantage over the pyramidal, and it would be well if the latter were adopted generally.

Higher Systems. With the exception of the classic work of van 't Hoff, investigations on systems containing more than four components have not very often been carried out to any degree of completeness. With a fifth component, the sum of the phases and degrees of freedom becomes seven, one more than in the quaternary systems. It is then no longer possible to represent all the phase relationships in a three-dimensional concentration figure unless some further limitation be introduced reducing the variability of the system.

Van 't Hoff's work dealt with aqueous solutions of salts, in particular with chlorides and sulphates of sodium, potassium and magnesium : in other words, with mixtures containing two negative and three positive radicals connected by the relation that the numbers of equivalents of each type of radical must be equal. His prime object was to study the conditions under which these salts, or compounds one

with another, separate during natural evaporation of such waters as those from which the successive layers at Stassfurt were deposited. These waters (for example, ordinary sea or salt-lake water) on evaporation first deposit sodium chloride, so that the salts which appear later separate from a solution which is at the same time saturated with sodium chloride. If one, then, lays down the condition that solid sodium chloride shall always be one of the phases present, such a system of two negative and three positive radicals in water may be regarded as one of only four independent components. The representation of isotherms by means of a space model then becomes possible.

It is only by such means, or under such limitations, that one may graphically set out the results of solubility investigations in systems of more than four components. It is beyond the scope of this book to discuss such salt work of the kind as has been carried out by van 't Hoff, Meyerhoffer and several other brilliant investigators. Any one interested in the matter is advised to read, apart from the original memoirs, a survey of work done on the oceanic salt deposits which was published by Ernst Jänecke in the *Zeitschrift für anorganische Chemie* for 1918.

CHAPTER VII

SOME THERMODYNAMICAL CONSIDERATIONS

The application of thermodynamics to equilibria of the types that have been considered can hardly be said to have led very far on the purely practical side. The generalizations which are obtainable contain functions the quantitative evaluation of which is not possible owing to the unknown

factors involved exceeding in number the known independent equations connecting them.

Apart, however, from the side of purely practical application, the generalizations are of high interest, and it is intended here to give briefly the chief of them and then to show in the next chapter how use may be made of certain of them from a qualitative standpoint. The discussion will, of necessity, be very slight, and students wishing to understand the subject thoroughly are advised to read Sackur's *Thermochemistry and Thermodynamics* (Macmillan & Co.), Partington's *Thermodynamics* (Constable & Co.), Planck's *Thermodynamik* (von Veit und Co., Leipzig), or Lewis's *System of Physical Chemistry*, vol. ii (Longmans & Co.).

The First Law. The first law of thermodynamics, in accordance with which all changes in heterogeneous systems take place, is a special case of the principle of the conservation of energy and is best expressed in the form

$$dQ = dU + dW.$$

Here dQ signifies a small amount of thermal energy absorbed by a system (though not the differential of a specific finite quantity Q*) which results in increasing its internal energy by dU and effecting an amount of external work dW, usually by expansion against pressure.

In any particular change the signs of these quantities may be positive or negative. It was supposed by Julius Thomsen (1851), Berthelot (1868) and others that in any change which occurred spontaneously without addition of energy from some external source, dQ must be negative: that is to say, heat must be evolved. They regarded the heat of reaction as a measure of the force driving the system towards its equilibrium state. The equilibrium

* See Planck, *Thermodynamik*, 4th edn., 1913, foot-note to p. 55.

conditions described in the foregoing chapters could be attained therefore only through exothermic actions. As a matter of fact, however, many quite common spontaneous chemical reactions are endothermic, or proceed with absorption of heat, and the number is greater at higher temperatures than at lower. Some other quantity than heat evolved must therefore be the factor determining the direction of an action, and the first law of thermodynamics does not suffice to indicate it.

The Second Law. From the second law, however, the conditions may be deduced under which a system will be in equilibrium either when completely isolated or, as is more usual in the cases which have been considered, when in some definitely prescribed relation to its surroundings.

The second law, which like the first has an empirical basis, may be regarded as being concerned with the possibility of converting heat into work. While in accordance with the first law a definite relation exists between heat and work, and while work may always be converted completely into heat, the reverse change of heat into work is never observed to be complete in any natural process. In other words, heat cannot, as a matter of experience, be converted into work as the one and only result of a spontaneous process. Some other change always occurs as well, and this change is thermodynamically irreversible. The raction of the total heat supply which may be converted into work* depends upon the particular process adopted, but there is a definite limit to it which cannot in any circumstances be exceeded. This limit is attained in a process which is at every stage reversible, in the sense

* This fraction is known as the 'efficiency' or the 'conversion ratio', alike of the process employed and of the machine which effects it.

in which the term 'reversible' is understood in thermodynamics.

Reversibility. A strictly reversible process in this sense is one which passes through a continuous series of equilibrium states. The driving force in such a case must be infinitesimally small, and this means that the velocity of the change will also be infinitesimal. In practice such processes are not realizable. In every spontaneously occurring natural process the driving force will be finite and the process therefore not completely reversible. The fraction of the heat of a given system which may be converted into work (and thence back into heat) will be a maximum, and the fraction spent irreversibly on other changes a minimum, in limiting cases to which one cannot in practice do more than approximate.

The nature of the machine * used in this conversion is immaterial so long as the condition of reversibility is observed. Any such machine must work between specific temperature limits, say T_1 and T_2 on the absolute scale. A quantity of heat, Q_1, will be taken in at T_1. A proportion of it will be converted into work, but it will be impossible to obtain work equivalent to a certain balance, Q_2, which must be given up at T_2, the lower limit of temperature at which the machine works.

From considerations of such cycles as that of Carnot it may be shown that

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \quad . \quad . \quad . \quad . \quad . \quad (1),$$

which means that of the total heat Q_1 taken in, the maximum fraction which may be converted into work is equal to the ratio of the temperature range over which the process

* The term 'machine' includes two essential elements; one is the working substance, the other is the mechanism by which it operates.

occurs to the temperature at which this quantity Q_1 was received.

The complete conversion of heat to work would be possible, therefore, only in the impracticable case of a machine working reversibly from T_1 to absolute zero. In this case only does the efficiency attain the value unity. The maximum efficiency between T_1 and any other temperature than zero is less than 1 ; and the relative efficiency of any process not completely reversible will be less than this maximum, that is

$$\frac{Q_1 - Q_2}{Q_1} < \frac{T_1 - T_2}{T_1} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Adequate discussion of these matters must be sought in the text-books cited, or others.

Entropy. Equation (1) may be written in the form

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0,$$

or if the heat absorbed, Q_1, be considered as positive, and heat given out, Q_2, as negative in sign,

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Where, however, the efficiency is less than the maximum possible, it follows from equation (2), introducing the same convention as to sign of Q, that

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This holds for any simple cycle, that is to say, for any cycle in which the addition or subtraction of heat takes place at two temperatures only. But it may readily be shown that any given cycle at all, such as that represented in Figure 106, from state A to state B along the path ACB and then back again to A along another path BDA, is equivalent to a sum of simple cycles, and the greater the

number of the simple cycles the more closely does their course approximate to the given one.

Hence in the limit, the equation (3), characteristic of a simple reversible transformation, becomes

$$\int \frac{dQ}{T} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5);$$

where the integral on the left is made up of two integrals,

$$\int_A^B \frac{dQ}{T} \text{ along the path } ACB, \text{ and } \int_B^A \frac{dQ}{T}$$

along the path BDA, which are therefore equal in magnitude and of opposite sign.

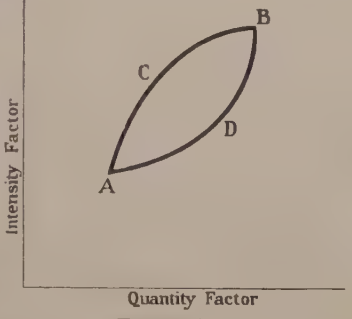


FIGURE 106.

Since these integrals are taken along different paths, their common magnitude must be independent of these paths, depending only upon the terminal states A and B. It therefore follows that either of these integrals represents a fundamental difference between the respective values, characteristic of the states A and B, of some function of the variables by which these states are defined. Writing this function as S we have

$$S_A - S_B = \int_B^A \frac{dQ}{T},$$

or

$$dS = \frac{dQ}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

To this function S the name 'entropy' is given. In a change which proceeds at every stage with maximum efficiency of conversion of heat to work (i. e. without irre-

versible change), to which, therefore, equation (3) applies at every stage, we may write, for each such stage,

$$\frac{dQ}{T} = 0, \text{ that is, } dS = 0.$$

Irreversible change. For every change, however, where the efficiency is not a maximum and where, therefore, equations (2) and (4) hold,

$$\int \frac{dQ}{T} < 0.$$

These are the kinds of change we find occurring spontaneously in nature, in the processes of solution, vaporization, crystallization, condensation and the like. In these, the driving force is not infinitesimal, and reversibility is not realized. If the change be from state A to state B, it follows then that nature has, so to speak, some 'preference' for state B, since the system passes to B spontaneously but cannot return from B to A without the expenditure of work upon it by some external agent.

Any quantity which gives a measure of this 'preference' will enable us to predict the direction of change between any two states. This quantity must be the difference between the values of some function for the respective states, a function which increases in all irreversible changes and remains constant in reversible ones. Such a function must also, of course, depend only upon the variables defining that particular state and be quite independent of the previous history of the system before it attained that state. Moreover, the function must be single-valued, that is, any possible set of simultaneous values of the variables must specify only one value of the function.

General condition for thermodynamic equilibrium. Berthelot's assumption that heat of reaction was the required quantity was incorrect because the amount of heat given

out in changing from state A to state B is dependent upon the path taken by the process of change, that is, upon the complete history of the final system from its initial to its final state. When, for example, zinc displaces copper, the heat of reaction may amount to a considerable positive quantity: but if the displacement be carried out in such a way that an electric current is produced, the residue of the energy change, which will appear as heat of reaction, may be negative.

The function entropy, however, does comply with all the necessary conditions prescribed in the previous section. $S_A - S_B$ is the difference of two values of this function, the magnitudes of which are dependent only upon those sets of values of the variables which define the states A and B, respectively.

From the equation

$$S_A - S_B = \int_B^A \frac{dQ}{T},$$

which defines entropy change, it is obvious that, when the right-hand side is zero, $S_A = S_B$, that is, in a reversible change, entropy remains constant. When, however, the change is partially or wholly reversible the right-hand side is negative, so that $S_A < S_B$, or the change from A to B results in an increase of entropy. This result is quite general for all isolated systems in which the changes which take place are entirely independent of any that may occur outside.

Restatement of laws. To the first law, that the total energy of an isolated system remains constant whatever changes may occur in it, we may now add the second law, in the form that spontaneous change in such a system will occur only when the result is an increase in entropy.

Limitations in practical application. It is clear that these two statements might be of the utmost importance in the practical quantitative consideration of heterogeneous systems. Whether, for example, a mixture of, say, two simple salts and water will, or will not, spontaneously change into a hydrated double salt and a solution when no energy is introduced from without or given out by the system, depends simply upon whether the sum of the entropies of the components before reaction is less or greater than the sum of those of the resultant phases, and this in turn greater or less than that of any other arrangement. If therefore one could calculate entropy from a knowledge of the variables, pressure, temperature and volume composition for any and every phase, one could always predict the direction and extent of a change.

Unfortunately it is not possible always to do this. For one thing, it follows from the definition of entropy as

$$\int \frac{dQ}{T}$$

that it contains an integration constant not determinable by thermodynamics which is, in part at least, characteristic of the substance or phase, but otherwise arbitrary. But quite apart from this, the integration as a function of the variables of condition is not possible unless an equation connecting them is known. For a perfect gas such an equation is known, and we may readily calculate the entropy of, say, a gramme-molecule, in the following manner:

In accordance with the first law, $dQ = dU + dW$. Hence

$$dS = \frac{dQ}{T} = \frac{dU + dW}{T}.$$

Now the increase per degree per gramme-molecule of the internal energy of the gas, being independent (by the Joule-Gay Lussac Law) of the volume, may be written

as $C_v dT$, where C_v denotes the molecular heat at constant volume. Also the work done, dW, may be written as pdv, hence

$$dS = C_v \frac{dT}{T} + \frac{pdv}{T},$$

or, since $pv = RT$,

$$dS = C_v \frac{dT}{T} + R \cdot \frac{dv}{v}.$$

Integrating, $$S = C_v \log T + R \log v + S',$$

where S' includes a constant characteristic of the gas, but is otherwise arbitrary.

Where therefore one is concerned only with changes in the same gas, as in expansions and compressions, differences in entropy may be calculated in terms of measurable quantities, R, v and T (the integration constants disappearing) and the direction of change predicted.

In the cases of liquids and solids, however, a general equation of condition is lacking, and we are unable from a knowledge of variables to predict whether, or in what direction, a given system will change.

Conditions of equilibrium in systems under constraint. The law that a system is in equilibrium only when its entropy has a maximum value holds only if the system be isolated in the sense indicated above. But to effect such isolation is extremely difficult, and, in practical investigations of phase equilibria, systems are usually subjected to some condition, such as constancy of temperature or pressure, which can be maintained only by changes in bodies exterior to the system. In every such case the condition for equilibrium is different. Writing the first law, $dQ = dU + dW$, in the form $TdS = dU + dW$, the equilibrium conditions in two cases of the kind may then be deduced in the following way:

I. *Isothermal isometric systems: free energy a minimum.* When the condition of constraint is that the temperature be maintained constant, the simple system may be regarded as part of an extended system, which includes a thermostat of such large mass and inexpansible material that, when it gives up or gains heat, it has no work done on it by, nor does it do any work against, its surroundings consequent upon its contraction or expansion. Hence, using partial differentials and representing the condition of constraint by a subscript symbol,

$$T(\delta S)_T = (\delta U)_T + (\delta W)_T,$$

By the second law, the system will be in equilibrium when it cannot do work upon its surroundings, that is, when its volume is maintained constant; for if any spontaneous change occurs in it, it must be such that if carried out reversibly it would do work. Hence $(\delta W)_T$ cannot be positive: it can only be zero or negative. Therefore $(\delta U)_T - T(\delta S)_T$, which is equal to $-(\delta W)_T$, must be either zero or positive. Putting

$$\psi = U - TS, \text{ or}$$
$$(\delta\psi)_T = (\delta U)_T - T(\delta S)_T,$$

it follows that the equilibrium condition is $(\delta\psi)_T \geqq 0$, which can be the case only when ψ is a minimum.

To ψ, defined by the equation above, the name of 'free energy' is given; whence it follows that *an isothermal isometric system is in equilibrium when its free energy is a minimum.*

II. *Isothermal isobaric systems: thermodynamic potential a minimum.* Isothermal isobaric systems are of the greatest practical importance. Temperature is maintained constant by means of a thermostat and the pressure is throughout that, say, of the atmosphere. The thermostat, as before, may be assumed of a kind which can give out or absorb

heat without doing work: a pressure regulator, thermally insulated from its surroundings, keeps the pressure constant at a value p. The simple system will now be in equilibrium when the extended system, comprising the simple one, the thermostat and the regulator, cannot do work upon the surroundings, that is, when the system does no work in excess of that done on the pressure regulator. The quantity dW in the original equation,

$$TdS = dU + dW,$$

must now be written in two parts, $p\,(\delta v)_{T,\,p}$ done on the regulator, and $(\delta W)_{T,\,p}$ done on the surroundings, or

$$T(\delta S)_{T,\,p} = (\delta U)_{T,\,p} + p\,(\delta v)_{T,\,p} + (\delta W)_{T,\,p}.$$

Then for equilibrium,

$$(\delta W)_{T,\,p} = 0 \text{ or is negative;}$$

therefore

$$(\delta U)_{T,\,p} + p\,(\delta v)_{T,\,p} - T(\delta S)_{T,\,p} \geqq 0.$$

Writing $\zeta = U + pv - TS$

and hence $(\delta\zeta)_{T,\,p} = (\delta U)_{T,\,p} + p\,(\delta v)_{T,\,p} - T(\delta S)_{T,\,p}$

this condition becomes

$$(\delta\zeta)_{T,\,p} \geqq 0.$$

To ζ, defined by the equation above, the name 'thermodynamic potential' is given; whence it follows that *an isothermal-isobaric system is in equilibrium when its thermodynamic potential is a minimum.*

By similar methods the corresponding conditions for equilibrium in isentropic and other systems may be deduced, but these are unimportant compared with the cases quoted.

The remarks already made respecting the impossibility of calculating entropy in the polyphase systems met with in practice apply both to free energy and thermodynamic potential. Their applications can therefore be only qualitative, but in the case of thermodynamic potential such

applications have proved of much value as general guides, since the equilibrium of heterogeneous systems is most readily amenable to experimental treatment when the systems are maintained at constant temperature and pressure. Heterogeneous equilibria of this type have therefore been the most fully investigated of all, as has been shown often enough in the preceding pages.

Hence some further consideration of this function is desirable in connexion with the specific types of system with the equilibria of which the phase rule deals, namely, homogeneous phases, such as solids, liquids and mixtures of gases, the state of which is determined only when pressure, temperature and composition are known.

Thermodynamic potential and phase composition. When, as is usual, temperature and pressure are maintained constant, interest centres round variations in composition; and it is desirable to seek an expression, in terms of the ζ-function and the concentrations of individual components, for the conditions determining such spontaneous variations. The procedure to be followed will be the same as that adopted in the deduction of the ζ-function. A chosen system, with the necessary thermostats and pressure regulators, will be considered to be isolated and the condition of equilibrium taken to be in accordance with the second law, that in which any deviation, if conducted reversibly, would require work to be done on the system by its surroundings.

As a simple and sufficient case, a system may be considered containing two homogeneous solutions A and B of different compositions, maintained by suitable arrangements at common temperature and pressure. The masses of the several components in A are A_1, A_2, A_3, ..., A_n, and the corresponding components in B, B_1, B_2, B_3, ..., B_n.

For these two solutions to attain equilibrium it may be necessary for one to receive from the other definite amounts of the various components. For simplicity it will be assumed that only one component passes from B to A, that is, that A_1 and B_1 vary while $A_2, A_3, \ldots, A_n$ and $B_2, B_3, \ldots, B_n$ remain constant. For the transfer of a small quantity δB_1 there will be a change in the sum of the energies U_A and U_B of the original systems, of the entropies S_A and S_B and the volumes V_A and V_B.

This change must be in accordance with the fundamental law $\delta Q = \delta U + \delta W$, or putting $\frac{\delta Q}{T} = \delta S$, and rearranging,

$$\delta U = T\delta S - \delta W.$$

W may be divided into two parts, namely, work done against the pressure regulators included in the system, and work done against surroundings. The complete expression for the energy change in this case is therefore given by

$$\delta(U_A + U_B)_C = T\delta(S_A + S_B)_C - p\delta(V_A + V_B)_C - (\delta W)_C,$$

where subscript C indicates constancy of T, p, $A_2 \ldots, A_n$ and $B_2, \ldots, B_n$. Rearranging terms,

$$\begin{aligned} -(\delta W)_C &= \delta(U_A - TS_A + pV_A)_C + \delta(U_B - TS_B + pV_B)_C \\ &= (\delta\zeta_A)_C + (\delta\zeta_B)_C, \end{aligned}$$

where ζ_A is the thermodynamic potential of the varied component in solution A and ζ_B of that in B.

These functions will be dependent, respectively, upon T, p and the masses of components, so that

$$d\zeta_A = \frac{\delta\zeta_A}{\delta T}.dT + \frac{\delta\zeta_A}{\delta p}.dp + \frac{\delta\zeta_A}{\delta A_1}.dA_1 + \ldots + \frac{\delta\zeta_A}{\delta A_n}.dA_n$$

and

$$d\zeta_B = \frac{\delta\zeta_B}{\delta T}.dT + \frac{\delta\zeta_B}{\delta p}.dp + \frac{\delta\zeta_B}{\delta B_1}.dB_1 + \ldots + \frac{\delta\zeta_B}{\delta B_n}.dB_n.$$

But the assumption has been made that the only variables are A_1 and B_1. Hence all the differentials vanish except

dA_1 and dB_1, where dA_1 is the amount of component (1) passing from B to A, written above as δA_1.

dB_1 is equal and of opposite sign, $-\delta A_1$. Hence

$$d\zeta_A = \frac{\delta \zeta_A}{\delta A_1} . \delta A_1$$

and

$$d\zeta_B = -\frac{\delta \zeta_B}{\delta B_1} . \delta A_1.$$

Therefore the value of $-(\delta W)_C$ becomes

$$\left(\frac{\delta \zeta_A}{\delta A_1} - \frac{\delta \zeta_B}{\delta B_1}\right)\delta A_1 ,$$

or, putting $\mu_{A_1} = \frac{\delta \zeta_A}{\delta A_1}$ and $\mu_{B_1} = \frac{\delta \zeta_B}{\delta B_1}$,

we have $$-(\delta W) = (\mu_{A_1} - \mu_{B_1})\, \delta A_1.$$

If now the passage of some B_1 to A_1, that is, the increase of A_1 by δA_1, occur spontaneously, δW, by the second law, must be positive.

Hence $\mu_{A_1} - \mu_{B_1}$ is negative since δA_1 is positive: therefore $$\mu_{B_1} > \mu_{A_1}.$$

Chemical Potential. To the quantity μ the name of 'chemical potential' is given and the result just obtained may be put in the following words:

For a component to pass spontaneously from one system to another the thermodynamic condition is that its chemical potential in the one be greater than that in the other. Hence, also, equilibrium in respect to any component is possible between two systems only when its respective chemical potentials in the two are identical.

The chemical potential $\frac{\delta \zeta}{\delta A_1}$ of a component A_1 of any system may be defined as the change in thermodynamic potential which the system suffers when, to a very large amount of it, there is added unit mass (gramme, gramme-molecule or other unit arbitrarily selected) of the component,

the pressure, temperature and masses of other components being kept constant, and the total amount of the system taken being so large that the added unit of mass is relatively negligible.

It was this quantity to which reference was made in the foot-note to p. 17, Chapter I. What were termed 'phase-equilibrium equations' in the deduction of the Phase Rule, were, fundamentally, expressions of the equalities of the chemical potentials possessed by any one component in the various phases present in equilibrium.

The theoretical significance of chemical potential is obviously very great: its practical quantitative application is not yet possible. For a thorough account of heterogeneous equilibria from the thermodynamical standpoint the student is referred to the original work of Willard Gibbs, *Scientific Papers*, i, pp. 62–100.

CHAPTER VIII

A DISCUSSION ON BINARY AND TERNARY SYSTEMS OF MIXED CRYSTALS WITH ILLUSTRATIONS OF THE GRAPHICAL USE OF THE ζ-FUNCTION.

Although thermodynamic potential, or as it is usually termed, the ζ-function, cannot be calculated quantitatively for such phases of matter as have been dealt with in earlier chapters, yet it is possible to make use of it qualitatively to reach certain general conclusions of considerable interest.

An appropriate example, which it is proposed to discuss in some detail, is its application as a guide to the possible types of mixed-crystal formation in binary systems. Before

passing, however, to this particular subject, attention will be directed to the very great theoretical significance, and the wide generality, of mixed-crystal (or solid-solution) formation.

Compositions of solid phases. Reference has already been made in the Preface to the fact that in a binary system, and also in higher systems, an alteration in composition of solid phase must be regarded as the invariable effect of an alteration in composition of liquid phase, if equilibrium between the two be maintained. This means, in effect, that for every series (or curve) of liquid solutions there corresponds an equally definite series (or curve) of solid solutions. In many cases the latter is so exceedingly short that experimental analysis fails to reveal it, and the curve is, for practical purposes, a point.

In Chapters IV, V and VI the question of composition of single-phase solids has been deliberately ignored, though, in ignoring this, it has frequently been impossible to avoid language not strictly justifiable. Thus, one has spoken of the single composition of a point in relations where a statement of a succession of compositions could alone be justified. To put the argument for this in a form rather different from that adopted in the Preface, it is only necessary to re-examine a couple of cases which have been considered, respectively, in Chapter IV (Figure 26, p. 74) and Chapter V (Figure 67, p. 120).

If it were strictly true that every solution along the curve *ECF* in Figure 26 could be in equilibrium with one and the same solid of composition C', it would follow that at a temperature such as r the two solutions t and l could coexist with one another. This, of course, is not so. In whatever proportions these two be brought together, a phase reaction occurs and a solid phase appears.

So, too, in Figure 67, if the solutions *a* and *b* on the curve *ed* could exist in equilibrium with precisely the same solid *S*, then they would be able to coexist with one another; and the same applies to all solutions along *ed*. They cannot do so. Again, if solution *e* were in equilibrium with the solids *A* and *S*, and solution *d* with the solids *S* and *C*, it would follow that a univariant condensed system of solution *e*, solution *d*, solid *A*, solid *S* and solid *C* (five phases in all) would be able to exist. This is in very definite contradiction to the Phase Rule, so that it is impossible to avoid the conclusion that the composition of a solid phase varies, however little, with that of the liquid with which it is in equilibrium.

The justification for the course that has been followed, in omitting any reference to slight changes in compositions of solids, lies in the fact that the student will probably find it easier to take that course and then amend (or add to) it in certain particulars than to take the strictly accurate course from the beginning.

The importance of a consideration of mixed crystals will now be apparent, though it will hardly be necessary to discuss a great number of examples. It will simplify matters to regard the pressure always as constant and sufficient to prevent vapour formation in all systems about to be mentioned, since alterations in equilibria between solids and liquids, brought about by small variations of vapour pressure, will be quite negligible: in other words, such systems may very reasonably be treated as 'condensed'.

A deduction of all the types for binary systems was first made by Roozeboom in a classic paper.* His deduction was based on a qualitative use of thermodynamic potential,

* *Zeit. phys. Chem.*, 1899, 30, 385.

and it is not possible to do better than to follow his method.

Binary Systems. At any temperature the thermodynamic potential for each possible mixture of any two components will have a definite value if the mixture be solid and another definite value if it be liquid. The equilibrium state will be that which possesses the minimum value of ζ. The two sets of values may at some given temperature be identical for all mixtures for such similar components as optical isomers, and they may be considerably alike for two components of equal melting-point: but in general they will differ more or less from one another. As a first simple case, it will be assumed that the curves connecting composition and ζ value for solid and liquid mixtures, respectively, are similar in form but not identical: also that the melting-points of the components differ, that of B being the higher. For brevity these two curves will be denoted by ζ_S for the solid, and ζ_L for the liquid, mixture.

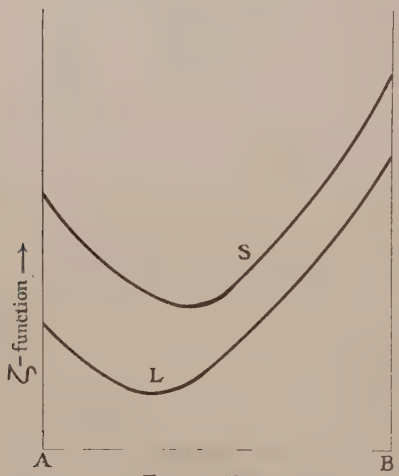


FIGURE 107.

For all temperatures above the melting-point of B, the ζ_S curve will lie wholly above ζ_L, as shown in Figure 107.

The thermodynamic potential of every mixture is here less in the liquid than in the solid state; that is to say, all mixtures are liquid or else metastable. With fall of tem-

perature, both sets of ζ values decrease, but ζ_S more than ζ_L. At the melting-point of *B*, where solid and liquid *B* are in equilibrium, the two curves start from the same point at 100 per cent. *B* as shown diagrammatically in section I (i) of Figure 109. All mixtures containing any *A* at all are liquid. At lower temperatures the ζ_S curve continues to fall more quickly than ζ_L, and between the melting-points of *B* and *A* cuts it progressively lower and lower, as shown in sections I (ii) and I (iii) of Figure 109.

The phase relationships in such cases may be deduced from the general diagrammatic type represented in Figure 108.

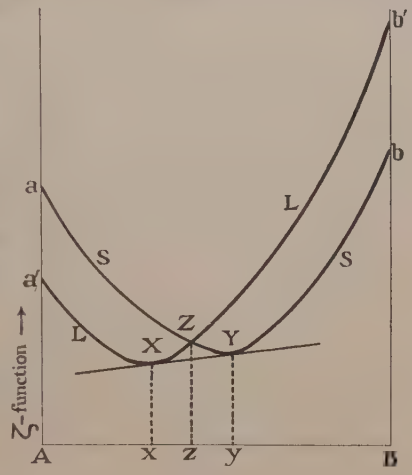


FIGURE 108.

It is at once apparent from this figure that the states represented by *aSZ* and *b'LZ* are unstable relatively to those of *a'XZ* and *bYZ*, respectively. At *Z* the thermodynamic potentials of solid and liquid mixtures of composition *z* are identical: hence these must exist in equilibrium. Therefore at this temperature all mixtures from *A* to *z* are liquid and from *B* to *z* are solid. The mixture *z* can exist as solid and as liquid, that is, this temperature is its melting-point.

But although *Z* represents an equilibrium state it is evident that the equilibrium is not stable. An infinitesimally small displacement along the ζ_S curve will not at

once be compensated by an equal and opposite displacement along the ζ_L curve: for although $\frac{\delta\zeta_S}{\delta C}$ (where δC is a small change in composition) might happen to be equal to $\frac{\delta\zeta_L}{\delta C}$, it has the opposite sign. Hence the change of thermodynamic potential brought about by the solidification of an infinitesimal amount of the liquid cannot be compensated by the melting of a corresponding amount of solid. On the contrary, any such solidification would at once upset the original unstable equilibrium, and the liquid and solid phases would pass in composition and thermodynamic potential to X and Y respectively. These points are those of contact of the common tangent to the ζ_S and ζ_L curves, and not necessarily the turning-points of the curves.

$$\frac{\delta\zeta_L}{\delta C} \text{ at } X = \frac{\delta\zeta_S}{\delta C} \text{ at } Y:$$

both are positive in the figure and the condition for stable equilibrium is attained.

Hence the possible systems from A to B at this temperature are the following:—From pure A to composition x all mixtures are liquid: from x to y there is a separation into phases, liquid of composition x and solid of composition y: from y to pure B all mixtures are solid. The proportions of the two phases separating between x and y are readily calculable: thus the mixture z would give zy/yx of liquid x and zx/xy of solid y.

At the melting-point of A the ζ_S curve lies wholly below ζ_L, the two starting from the same point at 100 per cent. A. For this temperature, section I (iv) of Figure 109 holds. Below it, pure components and all mixtures of the two can exist only as solids.

If now one plot for every temperature the compositions of the liquid and solid phases (such as x and y in Figure 108) in equilibrium at it, one obtains such a diagram as section I (vi) of Figure 109, a diagram the type of which may thus be deduced immediately from theoretical considerations of possible forms of the ζ-curves for solid and liquid mixtures. It shows a division according to temperature and composition into three fields. In the upper one all mixtures are homogeneous liquids. The middle one is bounded above by a curve for liquids (commonly termed the liquidus), below by one for solid phases (the solidus). Any mixture of composition and temperature represented by a point in it passes into a heterogeneous equilibrium between solid and liquid phases. At any point in the area below the solidus curve the conditions are such that only a (single-phase) solid solution can exist.

A comparison between this case and that of Figures 21 or 22 in Chapter IV will show the complete analogy which exists in two-component systems giving continuous series of equilibria between mixed crystals and liquids on the one hand and between liquids and vapours on the other.

If the set of curves in column I, Figure 109, has been understood, those in columns II and III will not offer difficulty.

In column II the ζ_S curve is more sharply rounded than the ζ_L curve: in III the opposite is assumed to be the case. Sections II (vi) and III (vi) give the deduced temperature-composition relations. Again the likeness to liquid-vapour systems of maximum and minimum boiling-points is clearly evident. The whole discussion of fractional distillation applied in the latter cases to the separation of the two components may be transferred, *mutatis mutandis*, to separation by fractional crystallization in the former.

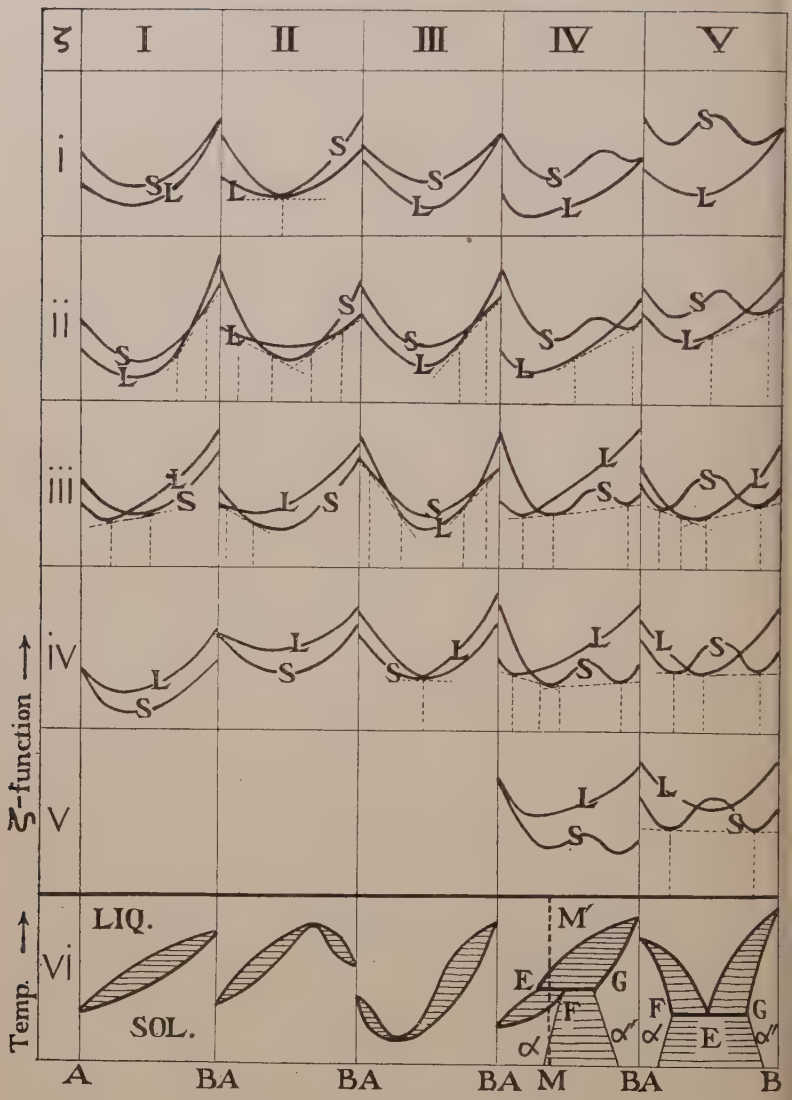

ζ
I
II
III
IV
V
i
ii
iii
iv
v
vi
ζ-function
Temp.
LIQ.
SOL.
S
L
M
E
G
F
α
α'
α''
A
BA
BA
BA M
BA
B

FIGURE 109.

In cases I, II and III of Figure 109 the curves ζ_S and ζ_L have been assumed to possess one turning-point only: but a case such as that represented in Figure 110 is clearly a possibility.

Here are two turning-points, and a similar argument to that applied to Figure 108 will show that if XY be the common tangent to the two sections, all mixtures between x and y, with ζ values lying on XZY, can be in unstable equilibrium only, the one possible stable state being the equilibrium between two phases of compositions x and y. The series of sections given in columns IV and V of Figure 109 show how one may deduce from the relative positions of ζ_S curves of this type and simple ζ_L convex curves two typical cases where gaps appear in the series of mixed crystals, that is, where the series is not continuous from A to B as in the cases I, II and III.

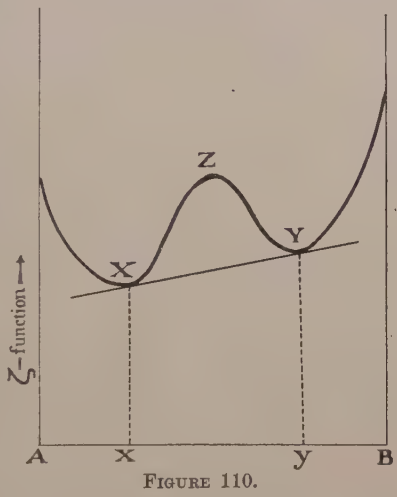


FIGURE 110.

In case IV the ζ_S curve is taken to be such that as it comes from above to below ζ_L, its two minima are on the B side of the minimum of the latter. The liquidus curve in IV (vi) of Figure 109 then shows a change of curvature at E, which is a transition temperature. There is a gap at this temperature in the solidus curve, and the solution E is in equilibrium with two solid mixed crystals of compositions

corresponding with F and G, respectively. Homogeneous single-phase mixed crystals cannot be formed from mixtures lying between F and G: at equilibrium there is a separation into two solid phases. In the figure this gap is assumed to widen with fall of temperature, and the areas between which it lies are marked α and α' to denote two different regions of miscibility.

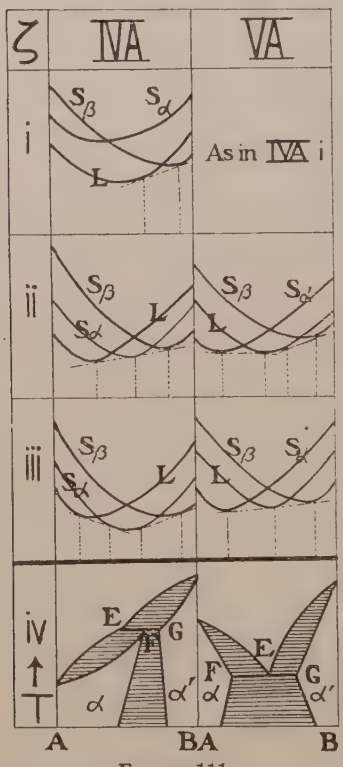


FIGURE 111.

In case V the ζ_S curve is assumed to be such that as it crosses ζ_L its minima lie on either side of the minimum of the latter. The liquidus curve, V (vi) in Figure 109, then shows a eutectic at E and again there is a gap in the miscibility of the solids.

These assumptions regarding the forms of the ζ_S and ζ_L curves have led to five types of composition-temperature diagram for two-component systems in which the solids may form mixed crystals. No types other than these are known, though IV and V may be obtained in different ways from those indicated, as for example when a melt may freeze to two kinds of mixed crystals. It will be a useful exercise for the student to follow the deductions of these curves from the ζ values

of the respective sets of solids and liquids in the way indicated in IV A and V A of Figure 111.

It will also be a good exercise in interpretation of diagrams to follow the changes in such a mixture as M in section IV (vi) of Figure 109 as the temperature is raised to M'. For a fuller treatment of the whole subject the original memoir of Roozeboom (loc. cit.) should be studied.

The possible cases of two gaps occurring in the series of mixed crystals should not be overlooked.

Ternary Systems. A similar graphical treatment of the ζ-function for other systems is possible, and for many ternary systems, both with and without mixed crystals, it has been worked out in a general way. A paper by van Rijn van Alkemade (*Zeit. phys. Chem.*, 1893, **10**, 289) on the subject is well worth reading. Numerous applications are discussed by Schreinemakers in Roozeboom's *Die heterogenen Gleichgewichte*, vol. iii, part ii, pp. 284 et seq. Representing compositions in a triangular diagram, the values of the ζ-function may be plotted upwards at right angles and will lie on a surface which may be convex or concave downwards or changing from one to the other. From the form of the surface the course of the isotherm may be deduced. Since little more than an illustration of the principle is aimed at here, no further discussion will be given along these lines; but it will be suitable just to follow this account of mixed crystals in binary systems with a short description of some of the many possible instances in ternary systems.

Since in each of the three binary systems possible with three components A, B and C, mixed crystals may, indeed must, be formed, there is, strictly speaking, only one case to consider. In practice, however, the variations from compositions of pure components may be of quite different

orders in the three cases: hence it is customary to distinguish three general types, namely:

I. One pair of components forms mixed crystals: the two others do not, or rather do so to an extent not perceptible experimentally.

II. Two pairs, respectively, form mixed crystals: the third not.

III. Each of the three pairs gives mixed crystals.

A fourth type is possible where none of the three binary systems may form mixed crystals to more than an inappreciable extent, but where these, if produced in recognizable amount, are always ternary in composition.

For the present purpose it is quite sufficient to discuss one type only, and No. I, being the simplest, will best serve in illustration. *A* and *C* will be taken as the one pair of components which can form mixed crystals. From what has been said above, it follows at once that there may be five sub-types corresponding with the five possible types of system which *A* and *C* may form. The first of these, where *A* and *C* form a continuous series of mixed crystals the melting-points of which lie between those of *A* and *C*, will be discussed fully, and references will be made to the second and third, where this series shows a maximum or minimum as the case may be.

A sketch of a solid model cannot very well be drawn to show clearly the variations of equilibrium from a temperature at which all mixtures are solid to one at which all are liquid, but the changes in these equilibria may be readily followed from Figure 112, where there are drawn isotherms at successive intervals of temperature.

No. i holds for temperatures below the melting-point of any stable solid, binary or ternary. All mixtures are therefore solid and at equilibrium are conglomerates of solid *B*

and mixed crystals of *A* and *C*. A mixture *a*, for example, consists of *ab/Bb* parts of solid *B* side by side with *aB/Bb* of mixed crystals containing *Cb/CA* of *A* and *Ab/CA* of *C*.

The lowest temperature at which a liquid can exist will be, say, the eutectic temperature of *B* and *C*, and immediately above it the isotherm will have the form of No. ii in Figure 112, and then in order iii, iv and v. Complexes falling within *ced* give only a single phase of unsaturated liquid. Along *ce* are the liquids saturated with solid *B*: along *de* those saturated with mixed crystals the compositions of which vary continuously from *C* to *f*. At *e*, therefore, is a liquid with which solid *B* and the mixed crystal *f* coexist, and

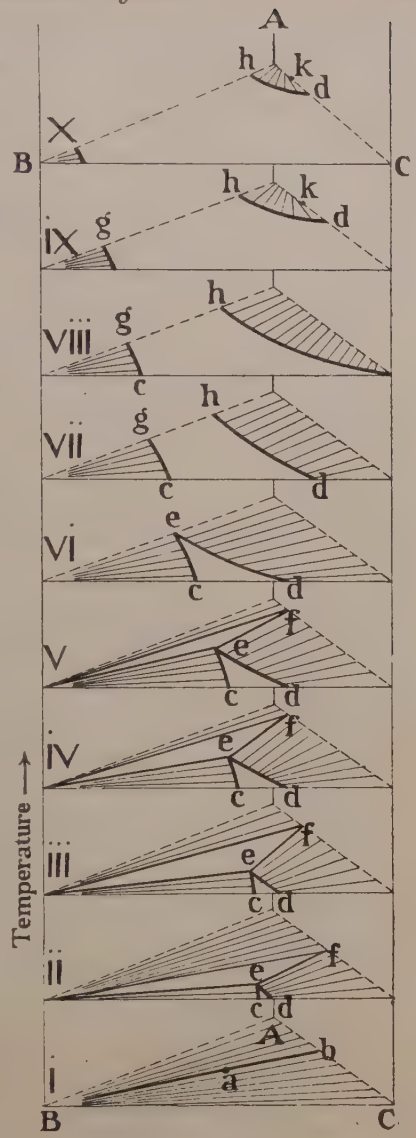


FIGURE 112.

any complex within the triangle *Bef* will separate into these three phases. This triangular area first increases in size and then diminishes, finally vanishing if and when *e* falls on *AB* as in No. vi. At the same time, the triangle *ABf*, the remnant of the system No. i, vanishes. When *e* lies on *AB*, the temperature is obviously that of the binary eutectic *A–B*. At this point the mixed crystals of *A* and *C* are in every case in equilibrium with respective liquids: in Nos. ii, iii, iv and v only one portion of the series was in equilibrium with liquids, the other being with solid *C*.

Further rise in temperature causes an increase in the unsaturated liquid area *ced* which becomes *cghd* and steadily spreads over the whole triangle. At some temperature *Bgc* will vanish, and at some other, above or below this, *AhdC* will also disappear after passing through the stages viii, ix and x. At the melting-point of *C*, assumed to be below that of *A*, *d* and *C* will coincide giving the isotherm No. viii. This is the highest temperature at which every stage of solid mixed crystal from *A* to *C* is possible. Above it, as in ix, some of the binary mixtures may be liquid only. Here *hd* gives the compositions of liquids coexisting with successive mixed crystals from *A* to *k*. Binary mixtures lying between *k* and *d* will not be solid, but will separate into liquid of composition *d* and the solid mixed crystal *k*. From *d* to *C*, all mixtures are liquid. Ultimately *h*, *k* and *d* all coincide at *A*, and above this temperature no solid phase is possible with any proportions of the three components.

If now, however, instead of the binary system *A–C* giving a continuous series as in column I of Figure 109, it gives that of Figure 113, the ternary isotherms become somewhat modified.

Instead of *e*, in Figure 112, meeting *AB* as in isotherm No. vi, between *A* and *B*, it will reach it only at *A*, and

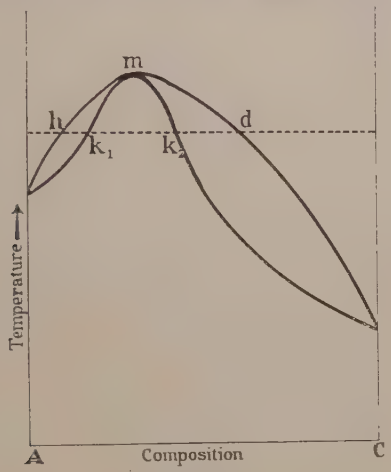


FIGURE 113.

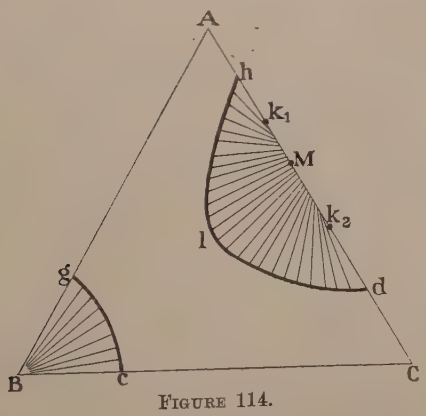


FIGURE 114.

then at a temperature above this the isotherm will be of the type shown in Figure 114.

The curve of liquids in equilibrium with mixed crystals is now *hld*, both ends being on the binary system *A*–*C*, as shown in Figure 113. The series of the mixed crystals runs only from k_1 to k_2 (see both Figures 113 and 114). *h*, k_1, k_2, *d* and all points on *hld* steadily approach one another, and at the temperature of *m* (Figure 113) the area *hld* vanishes to the point *M* in Figure 114.

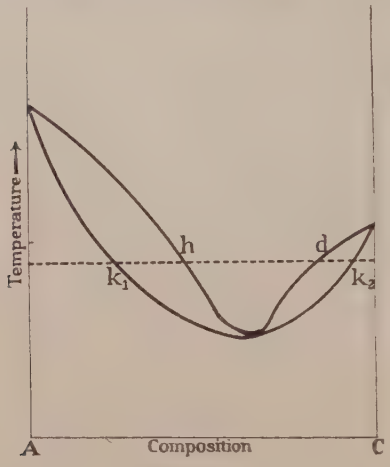


FIGURE 115.

Where, on the other hand, the binary system is that of Figure 115, it will easily be seen that Figure 116 is the ternary isotherm for a temperature below the melting-points of *A* and *C* but above the respective eutectics of *A*–*B* and *B*–*C*.

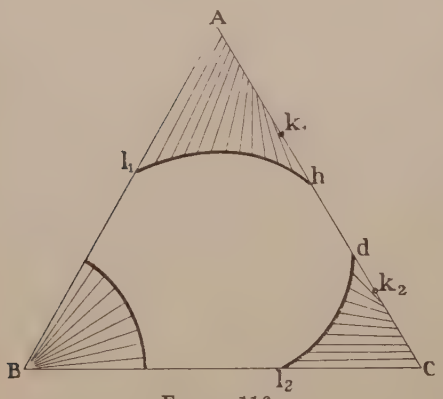


FIGURE 116.

Here mixed crystals can occur only from *C* to k_2 and from *A* to k_1. The corresponding liquids lie along $l_2 d$ and

l_1h, respectively. With rise of temperature the area l_1hA diminishes and vanishes at A, l_2dC at C.

One other point is worth noting. Returning to Figure 112, isotherms ii to v, it will be seen that as e moves from BC to BA, it traces out what is really a ternary freezing-point curve. Such a curve may have a maximum or a minimum or neither, and in the subsequent stages of Figure 112 it was assumed to have neither. If, however, it has a maximum, then before the side BA is reached there will be stages of the type represented in Figure 117.

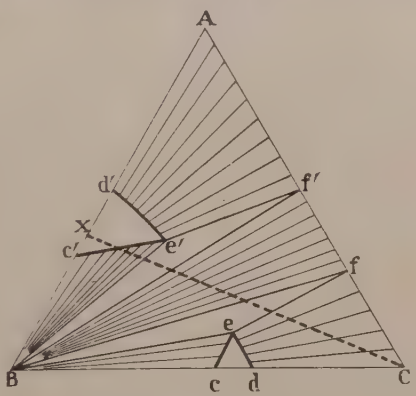


FIGURE 117.

At the maximum point, e and e' will meet and the isotherm thereafter will resolve itself into that of No. vii, Figure 112. The various areas in Figure 117 correspond with the following systems:

ced and *c′e′d′*	unsaturated liquids:
Bce and *Bc′e′*	solid *B* and solutions:
Cfed and *Af′e′d′*	mixed crystals and solutions:
Bff′	mixed crystals and solid *B*:
Bfe and *Bf′e′*	solid *B*, mixed crystal and solution.

This is an interesting system in which to trace the changes in phase which follow changes in composition. One may at once read from the isotherm the successive equilibria which follow additions of C to a mixture of A and B of composition given, say, by the point x. One may

also observe that addition in suitable proportions of unsaturated liquids in the areas *ced* and *c′e′d′*, respectively, may yield a mixture of mean composition lying in *Bf′f*, which will be entirely solid, containing the two phases *B* and mixed crystals of composition between *f* and *f′*.

When, on the other hand, the ternary freezing-point curve has a minimum, then just above this the isotherm has the form of Figure 118.

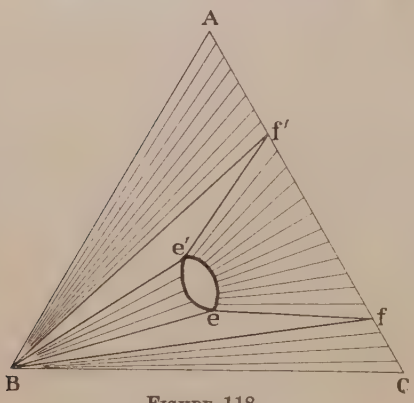


FIGURE 118.

The area of unsaturated liquids is now that lying between *e* and *e′*: along its one boundary the solid phase in equilibrium is *B*, along the other, mixed crystals from *f* to *f′*. The rest of the figure requires no explanation.

These indications will serve to give an idea of the types of isotherm met in these ternary systems where mixed crystals may appear. It is obvious that a complete discussion would be very lengthy, for the binary types IV and V of Figure 109 remain to be introduced into the ternary type I, while all five types, or combinations of them, are possible with ternary types II and III as well.

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